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Delivery Order 0018: Single Ion Conducting Solid-State Lithium Electrochemical Technologies (Task 4)

Sarwan S. Sandhu

University of Dayton Research Institute

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AIR FORCE RESEARCH LABORATORY
PROPULSION DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7251
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

NOTICE AND SIGNATURE PAGE

*//Signature//

JOSEPH P. FELLNER
Senior Chemical Engineer
Thermal & Electrochemical Branch
Energy/Power/Thermal Division

//Signature//

THOMAS L. REITZ, Chief
Thermal & Electrochemical Branch
Energy/Power/Thermal Division
Propulsion Directorate

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14. ABSTRACT
A theory-based mathematical model has been developed to quantitatively describe the electrokinetic and transport processes that take place in a lithium-based cell/battery during its operation. Future numerical simulation, based on the presented model formulation, of a lithium-based cell/battery is expected to provide the quantitative information for rapid cell/battery construction and experimental work. Performance of an operating cell/battery of a given design can also be predicted using the presented formulation.

15. SUBJECT TERMS
lithium battery, mathematical model, dilithium phthalocyanine, solid state diffusion, transport, electrokinetic

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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

Anode	lithium metal thin sheet or foil of thickness, l^A
Cathode	composed of an active material, such as lithium metal phthalocyanine, Li_xM_yPc (e.g., Li_xFePc or Li_xLi_2Pc), electrolyte $LiBF_4$ in the microporous poly(ethylene oxide) polymer, and acetylene black as the cathode electronic conductor of thickness, l^C
Cathode current collector	a metal, such as aluminum (Al), of thickness, l^{CC}
Electrolyte separator	solid polymer electrolyte, i.e., $LiBF_4$ in the microporous poly(ethylene oxide) polymer of thickness, l^S

1. SUMMARY

This technical report summarizes the theory based mathematical models, describing various processes that occur in an operating lithium-based cell. Such models provide the guidelines for cell/battery design improvement; leading to the experimental work reduction to attain a desired cell design for optimum cell performance. The developed formulation covers the following sub topics:

1.1 Cathode Formulation

The developed mathematical expressions describe the transient intercalated lithium concentration profiles in the cathode particles of an active material, for example, FePc (iron phthalocyanine), transient cathode current and charge storage during the cell discharge period. Voltage loss associated with the lithium ion and electron transport in the cathode composite of electrolyte, carbon black and active material can be estimated. Based on the thermodynamic equilibrium condition for the electrochemical reaction at the electrolyte-active material interface, a mathematical equation relates the cathode reaction reversible electric potential to the lithium content of the cathode electrode. Based on the fundamentals of electrode kinetics, the cathode active material-electrolyte interfacial current density has been quantitatively related to the cathode active material lithium content, lithium ion concentration in the electrolyte, the surface overpotential and the cathodic reaction exchange current density.

1.2 Electrolyte Separator Formulation

To compute the voltage drop in the separator, e.g., $LiBF_4$ in microporous poly(ethylene oxide), between the cell electrodes, a relatively simple mathematical expression is provided.

1.3 Anode Formulation

The electrokinetics of the lithium metal sheet in contact with the electrolyte has been modeled to predict the interfacial current density. The interfacial current density is expressed in terms of the anode exchange current density and the surface overpotential at a given temperature at the anode-electrolyte interface. A developed mathematical expression relates the reversible electric potential of the anode reaction to its standard-state electric potential and the lithium ion activity in the electrolyte at the lithium anode-electrolyte interface.

1.4 The Lithium-Based Cell Reversible Electric Potential Formulation

The developed formulation relates the reversible cell potential to the lithium activity in the cathode active material, e.g., lithium in M_yPc (e.g., FePc). Using the developed mathematical expression, one can develop semiempirical relation between the lithium activity in the cathode active material and lithium content of the cell cathode from the experimental data on the cell reversible voltage versus the cell lithium content. Such an empirical relation, in turn, may be used to predict the actual cell voltage during the cell discharge period.

1.5   Cell Performance Formulation

The actual cell voltage, electric power and thermodynamic efficiency are predicted during a given cell discharge period.

1.6   Cathode Active Material Spherical Particle Utilization to Store Lithium during the Cell Discharge Period

The developed formulation predicts the transient lithium concentration profile in a spherical particle of the cathode active material. The formulation was developed for a constant active material-electrolyte interfacial current density with the assumption of lithium diffusion inside a spherical particle of the cathode active material controlling the overall cathode and, hence, the overall cell performance during the cell discharge period. Furthermore, a developed mathematical expression predicts the cathode active material utilization or its coulomb efficiency until the lithium concentration in the cathode active material phase at its interface with electrolyte phase reaches the saturation level when the actual cell voltage rapidly decreases.

1.7   Voltage Loss associated with the Diffusion Transport of Lithium in the Cell Cathode Active Material

The Nernst-Einstein relation linking the lithium-ion mass diffusivity and its ionic conductivity was employed to develop a mathematical expression for the prediction of transient voltage loss associated with the lithium diffusion in the cell cathode active material.

1.8   Effect of Lithium Storage on the Cell Reversible Voltage

This sub section briefly describes the relation showing the transient effect of lithium storage in the cathode active material on the cell reversible voltage during the cell discharge period.

1.9   Further Treatment of the Reversible Potential of the Lithium-Based Cell

The liquid-phase electrolytic solution theory has been extended to account for the nonideal behavior of the solid-state cathode active material containing the intercalated lithium in it through the relation between the lithium ion content of the cathode active material and lithium activity coefficient. This information, in turn, has been related to the cell reversible voltage.

1.10   Fractional Utilization of a Cathode Active-Material Particle as a Function of Time

In this brief sub section, the formulation has been provided to compute the fractional utilization of the cathode active material in a spherical particle as a function of time at a constant active material-electrolyte interfacial current density during the cell discharge period.

2. INTRODUCTION

The lithium-based battery development is being pursued for aerospace, defense, medical, and hybrid electric and battery electric vehicle applications. Lithium-based storage devices also provide power for laptop computers, cellular phones, camcorders, etc. In the excellent review on lithium batteries and cathode materials [1], it has been stated that the layered oxides, e.g., $Li_xNi_{0.4}Mn_{0.4}Co_{0.2}O_2$, continued their current improvement with mixed transition metals slowly replacing the pure cobalt system (i.e. $LiCoO_2$) as the cathode materials for the lithium-based batteries. They are expected to offer enhanced safety with enhanced capacity at a lower cost. The first potentially low-cost cathode material appears to be the lithium iron phosphate ($LiFePO_4$). This will be achieved only if the costs of the other cell components are also reduced. These include the electrolyte, a lower cost anode with enhanced safety features that include the use of graphite and the use of 'thicker cathodes' to reduce the cost of electrode support materials, separators, etc. Metal phthalocyanines (e.g., $Li_2Pc[Li_2C_{32}H_{16}N_8]$, [2]) are also being investigated as low cost cathode materials.

Cost, specific energy, power, cycle life, calendar life, and safety are important factors that must be considered while deciding a lithium-based system for a particular application. Selection of component materials would decide cost and life of a lithium-based system. The required specific energy and power of a battery depend on the cell design. Experimental determination of an optimum cell design to provide a desired cell performance requires an intensive work that involves fabricating lithium-based cells of various designs, e.g., various insertion electrode compositions (such as the intercalated lithium metal oxide, lithium metal, intercalated lithium-in carbon, etc.), their thicknesses, void fractions, electrode active material particle sizes, an electrolyte composition, and thickness of an electrolyte-containing separator between the cell electrodes. Theory based mathematical models, describing various processes which occur in an operating lithium-based cell, are very helpful in providing the guidelines for cell/battery design improvement; leading to the experimental work reduction to attain a desired cell design.

A typical lithium-based cell, lithium | electrolyte $LiBF_4$ in poly(ethylene oxide) | intercalated lithium in M_yPc, is shown in Figure 1.
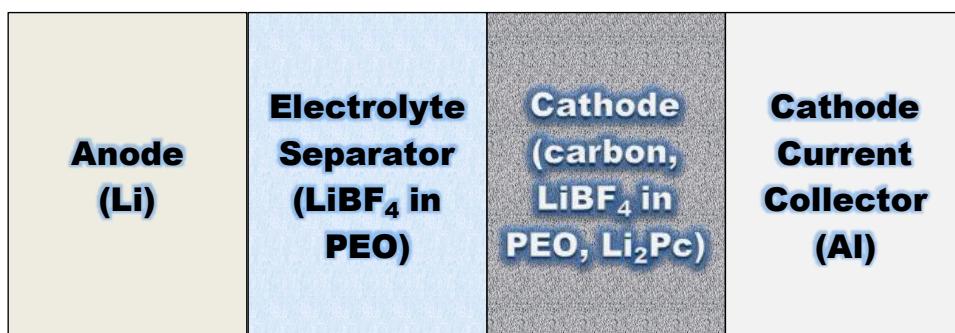
Figure 1.   Sketch of a lithium-based cell (not to a scale).

The various cell components, such as the anode, electrolyte separator, cathode and cathode current collector, shown in Fig. 1, are explained in the List of Acronyms, Abbreviations, and Symbols.

3. METHODS, ASSUMPTIONS, AND PROCEDURES

The mathematical model formulation of a lithium-based cell developed using the principles of thermodynamics, transport phenomena, and electrochemical kinetics is presented in the next section.

4.   RESULTS AND DISCUSSION

4.1   Mathematical Model Formulation

4.1.1   Cathode Formulation

It is assumed that the lithium ion transport through the solid electrolyte to the active material particles of metal phthalocyanine such as iron phthalocyanine (FePc) or dilithium phthalocyanine is much faster than the lithium ion diffusion in the active material particles of the cell composite cathode. A lithium ion on its arrival at the three phase interface between the electrolyte, metal phthalocyanine (M_yPc), and carbon black of electronic conductivity much higher than that of M_yPc undergoes a fast electrochemical reaction: $Li^+ + e^-$ □   ($Li \equiv Li^+ + e^-$ in the cathode active material). Then, lithium (as ($Li^+ + e^-$)) is assumed to enter a channel between two layers of M_yPc and diffuses in a solid-state cathode particle of M_yPc during the period of lithium storage in the cathode material, i.e. during the cell discharge period. The overall process of lithium storage in the cathode active material is assumed to be controlled by the lithium diffusion in the cathode M_yPc particles. The lithium accumulation is assumed to take place under the transient, isothermal and isobaric conditions. The differential model equation describing the lithium diffusion and accumulation in a spherical, active material particle is represented by the following derived equation:

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r^2}\left(r^2 D \frac{\partial c}{\partial r}\right) \tag{1}$$

where c = molar concentration of accumulating or intercalating lithium, D = molecular mass diffusivity of lithium in the active material particles. The initial and boundary conditions to solve the partial differential equation (1) are:

The initial condition, $t = 0$; $c = c_1$, initial uniform concentration of lithium in the cathode active material channels in a spherical particle of radius, a.

The boundary conditions for $t > 0$:

At the spherical particle center, i.e., at $r = 0$, c has a finite value; and at the particle surface, i.e. at $r = a$, $c = c_o$.

For the assumption of $D = \bar{D}$ (composition averaged diffusivity) = constant, the partial differential equation (1) becomes

$$\frac{\partial c}{\partial t} = \bar{D}\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{2}$$

The analytical solution of the differential equation (2) using the above mentioned boundary conditions [3] leads to:

$$\left(\frac{c-c_1}{c_o-c_1}\right)=1+\left(\frac{2}{\pi}\right)\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n}\left[\frac{\sin\left(\frac{n\pi r}{a}\right)}{\left(\frac{r}{a}\right)}\right]\exp\left[-\frac{\bar{D}n^2\pi^2 t}{a^2}\right] \qquad (3)$$

The transient concentration at the particle center can be obtained from Eq. (3) using L'Hôpital's rule:

$$\left[\left(\frac{c-c_1}{c_o-c_1}\right)\right]_{\text{at } r=0}=1+2\sum_{n=1}^{n=\infty}(-1)^n\exp\left[-\frac{\bar{D}n^2\pi^2 t}{a^2}\right] \qquad (4)$$

The dimensionless radial distance, ξ, and the dimensionless time, τ, are now defined as

$$\xi=\frac{r}{a} \qquad (5)$$

and

$$\tau=\frac{\bar{D}t}{a^2} \qquad (6)$$

The equations (3) and (4) are now expressed as

$$\left(\frac{c-c_1}{c_o-c_1}\right)=1+\left(\frac{2}{\pi}\right)\sum_{n=1}^{n=\infty}\frac{(-1)^n}{n}\left[\frac{\sin\left(n\pi\xi\right)}{\xi}\right]\exp\left[-n^2\pi^2\tau\right] \qquad (7)$$

$$\left[\left(\frac{c-c_1}{c_o-c_1}\right)\right]_{\text{at } \xi=0}=1+2\sum_{n=1}^{n=\infty}(-1)^n\exp\left[-n^2\pi^2\tau\right] \qquad (8)$$

To predict the stored or intercalated lithium concentration in a spherical particle of a cathode active material for short times, the following equation may be used.

$$\left(\frac{c-c_1}{c_o-c_1}\right)=\frac{1}{\xi}\sum_{n=1}^{n=\infty}\left\{erfc\frac{(2n+1)-\xi}{2\sqrt{\tau}}-erfc\frac{(2n+1)+\xi}{2\sqrt{\tau}}\right\} \qquad (9)$$

where

$$erfc\left[\frac{(2n+1)-\xi}{2\sqrt{\tau}}\right]=1-erf\left[\frac{(2n+1)-\xi}{2\sqrt{\tau}}\right] \qquad (10)$$

$$erfc\left[\frac{(2n+1)+\xi}{2\sqrt{\tau}}\right] = 1 - erf\left[\frac{(2n+1)+\xi}{2\sqrt{\tau}}\right] \tag{11}$$

where

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_{u=0}^{u=x} e^{-u^2} du \tag{12}$$

$$erfc(0) = 1, \; erfc(\infty) = 0 \tag{13}$$

Equations (7) and (9) can be used to predict $\left(\dfrac{c - c_1}{c_o - c_1}\right)$ as a function of (τ and ξ). Equation (8)

can be used to predict $\left(\dfrac{c - c_1}{c_o - c_1}\right)\Big|_{\xi=0}$ as a function of τ.

The total flux of lithium into a spherical particle of radius, a, at any time is given by

$$\dot{N}^t_{particle-flux} = 4\pi a^2 \left[\bar{D}\left(\frac{\partial c}{\partial r}\Big|_{r=a}\right)\right] \tag{14}$$

The mathematical expression for $\left(\dfrac{\partial c}{\partial r}\Big|_{r=a}\right)$ was obtained from Eq. (7) and substituted into Eq.

(14) to obtain

$$\dot{N}^t_{particle-flux} = \left[(8\pi a\bar{D})(c_o - c_1)\right]\sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\tau) \tag{15}$$

The lithium *g-atom* balance was applied over a spherical particle to obtain the following expression for the determination of stored or intercalated lithium at any time during the cell discharge period,

$$\int_{N^t=N^t_o}^{N^t=N^t} dN^t = \left(N^t - N^t_o\right) = \int_{t=0}^{t=t} \dot{N}^t_{particle-flux} dt \tag{16}$$

The use of Eq. (15) in Eq. (16) leads to:

$\left(N^t - N^t_o\right) = $ (amount of lithium stored in a particle of the cell cathode active material in time,

$\tau = \dfrac{\bar{D}t}{a^2}$)

$$\left(N^t - N^t_o\right) = \left[\frac{4}{3}\pi a^3 \left(c_o - c_1\right)\right]\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left\{\frac{exp\left(-n^2\pi^2\tau\right)}{n^2}\right\}\right] \tag{17}$$

In Eq. (17), $N^t_o = g\text{-}atom$ (or $g\text{-}mole$) of lithium in a spherical particle of the cathode active material just before the cell discharge to store or intercalate lithium into the cell cathode and provide electric power to an external circuit. The total amount of lithium, N^t, present in the active material particle until time, τ, is given by

$$N^t = N^t_o + \left[\frac{4}{3}\pi a^3 \left(c_o - c_1\right)\right]\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left\{\frac{exp\left(-n^2\pi^2\tau\right)}{n^2}\right\}\right] \tag{18}$$

As $t \to \infty$, therefore, $\tau \to \infty$; Eq. (18) reduces to

$$N^t_\infty = N^t_o + \frac{4}{3}\pi a^3 \left(c_o - c_1\right) \tag{19}$$

For the situation of 'no-storage' of lithium in the cathode active material channels before the cell discharge, the initial concentration of lithium, $c_1 = 0$ and $N^t_o = 0$; then, Eqs. (18) and (19) reduce, respectively, to

$$N^t = \left(\frac{4}{3}\pi a^3 c_o\right)\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left\{\frac{exp\left(-n^2\pi^2\tau\right)}{n^2}\right\}\right] \tag{20}$$

$$N^t_\infty = \frac{4}{3}\pi a^3 c_o \tag{21}$$

The active material channel-stored lithium concentration, c, is related to

$x = \dfrac{g\text{-}mole \text{ of the channel-stored or intercalated lithium}}{g\text{-}mole \text{ of the cathode active material at its initial state}}$ by the following equation:

$$c = \left(\frac{\rho_{M_yPc, o}}{M_{M_yPc}}\right)x \tag{22}$$

where $\rho_{M_yPc, o}$ = density of a cathode active material, e.g., FePc or Li_2Pc; and M_{M_yPc} = molecular weight of M_yPc. For the situation of cathode active material expansion during the cell discharge period, the channel-stored or intercalated lithium concentration c and x are related by the following equation

$$c = \frac{\rho_{M_yPc, o}}{M_{M_yPc}} \left(\frac{x}{1+\alpha x} \right)$$

(23)

where $\rho_{M_yPc, o}$ = density of the cathode active material when the channel-stored lithium concentration is zero, i.e. $x = 0$; and α = coefficient of the active material particle volume expansion.

The factor $(1+\alpha x)$ in Eq. (23) is related to the active material density by the following equation

$$\frac{(1+\alpha x)}{1} = \frac{\rho_{M_yPc, o}}{\rho_{M_yPc}}$$

(24)

where ρ_{M_yPc} = density of the 'initial' active material, M_yPc, when the active material channel-stored lithium content is x.

If the initial stored lithium, x_{ini}, were known; then, the initial concentration , c_1, of the intercalated lithium may be computed from

$$c_1 = \frac{\rho_{M_yPc, o}}{M_{M_yPc}} \left(\frac{x_{ini}}{1+\alpha x_{ini}} \right)$$

(25)

If it is assumed that the stored or intercalated lithium in a cathode active material particle at the particle-electrolyte interface, c_o is equal to $c^{sat'd}$, the stored lithium concentration when the active material channels are full of lithium; then c_o can be determined from

$$c_o = c^{sat'd} = \frac{\rho_{M_yPc, o}}{M_{M_yPc}} \left(\frac{x^{sat'd}}{1+\alpha x^{sat'd}} \right)$$

(26)

The active material, lithium-diffusion controlled current per active material particle of radius, a, is given by

$$I_p^C = F\dot{N}^t_{particle-flux}$$

(27)

Using the information in Eq. (15) for $\dot{N}^t_{particle-flux}$, Eq. (27) leads to:

$$I_p^C = F\left\{8\pi a\bar{D}\left(c_o - c_1\right)\right\} \sum_{n=1}^{n=\infty} \exp\left(-n^2\pi^2\tau\right), [A]$$

(28)

where F = Faraday's constant = $96487 C/g\text{-}equiv.$

The cathodic current per unit external surface area of an active material particle of initial radius, $a_{pi,o}$, is given by

$$i_p^C = \left(\frac{2F}{a_{pi,o}} \right)(1+\alpha x)^{-\frac{1}{3}} \bar{D}(c_o - c_1) \sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\tau), \left[\frac{A}{cm_s^2} \right]$$ (29)

For the situation of constant active material particle volume (i.e. $\alpha = 0$), Eq. (29) becomes

$$i_{p,\alpha=0}^C = \left(\frac{2F}{a_{pi,o}} \right)\bar{D}(c_o - c_1) \sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\tau), \left[\frac{A}{cm_s^2} \right]$$ (30)

For short times, the cathodic current per unit external surface area of an active material particle, $i_{p,short}^C$, is given by

$$i_{p,short}^C = \frac{F\bar{D}(c_o - c_1)}{a_{pi,o}}(1+\alpha x)^{-\frac{1}{3}} \sum_{n=0}^{n=\infty} \left[erfc\left(\frac{n+1}{\sqrt{\tau}} \right) - erfc\left(\frac{n}{\sqrt{\tau}} \right) + \left(\frac{e^{-n^2/\tau} + e^{-(n+1)^2/\tau}}{\sqrt{\pi\tau}} \right) \right], \left[\frac{A}{cm_s^2} \right]$$ (31)

The diffusion-controlled cathodic current per unit initial mass of the active material particles of radius, $a_{pi,o}$, is given by

$$I_{p, \text{per unit mass}}^C = \frac{I_p^C}{\left(\frac{4}{3}\pi a_{pi,o}^3 \right)\rho_{M_y Pc,o}}$$ (32)

or

$$I_{p, \text{per unit mass}}^C = \left(\frac{6F\bar{D}}{\rho_{M_y Pc,o}} \right)\left[\frac{(c_o - c_1)_i}{a_{pi,o}^2} \right]\sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\tau_{pi,o}),$$

$$\left[\frac{A}{gm \text{ of active material particles of initial size } a_{pi,o}} \right]$$ (33)

for the assumption of $\alpha = 0$, where $\tau_{pi,o} = \frac{\bar{D}t}{a_{pi,o}^2}$.

For the situation of the cathode active material particle volume change, $I_{p, \text{per unit mass}}^C$ per unit initial cathode active material mass may be estimated from the following equation:

$$I_{p, \text{ per unit mass}}^{C} = \left(\frac{6F\bar{D}}{\rho_{M_yPc,o}} \right) \frac{(c_o - c_1)_i (1+\alpha x)^{\frac{1}{3}}}{a_{pi,o}^2} \sum_{n=1}^{n=\infty} \exp\left(\frac{-n^2\pi^2\tau_{pi,o}}{(1+\alpha x)^{\frac{2}{3}}} \right) \qquad (34)$$

The total transient cathodic current associated with the active material particles of size, $a_{pi,o}$, present in the entire cathode is given by

$$I_{m_{pi}}^{t,C} = \left(\frac{6F\bar{D}m_o^{t,C}}{\rho_{M_yPc,o}} \right) \left(\frac{w_{pi,o}(c_o - c_1)_i}{a_{pi,o}^2} \right) \sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\tau_{pi,o}), [A] \qquad (35)$$

where $m_o^{t,C} = $ initial amount of active material particles of all sizes in the cell cathode when the channel stored lithium amount is zero, i.e., $x = 0$; and $w_{pi,o} = $ mass fraction of active material particles of radius, $a_{pi,o}$; if there were 'no intercalated lithium' in the cathode active material particles.

If the presence of different active material particle size ranges is accounted for, the total lithium-diffusion controlled current in the cell cathode is given by

$$I^{t,C} = \left(\frac{6F\bar{D}m_o^{t,C}}{\rho_{M_yPc,o}} \right) \sum_{i=1}^{i=N_p} \left[\frac{w_{pi,o}(c_o - c_1)_i}{\bar{a}_{pi,o}^2} \sum_{n=1}^{n=\infty} \exp(-n^2\pi^2\bar{\tau}_{pi,o}) \right], [A] \qquad (36)$$

In Eq. (36), $N_p = $ total number of size ranges of the active material particles present in the cathode, $\bar{a}_{pi,o} = $ surface-area fraction mean particle radius of the active material particles of the particle size range i, and $\bar{\tau}_{pi,o} = \dfrac{\bar{D}t}{\bar{a}_{pi,o}^2}$ (dimensionless time associated with $\bar{a}_{pi,o}$).

The total amount of charge stored in the cathode active material particles in time t during the cell discharge period is given by

$$Q^t - Q_o^t = \int_{Q_o^t}^{Q^t} dQ^t = \int_0^t I^{t,C} dt \qquad (37)$$

The substitution for $I^{t,C}$ from Eq. (36) into Eq. (37) and the integration of the resultant expression leads, on simplification, to:

$$\Delta Q^t = Q^t - Q_o^t = \left(\frac{Fm_o^{t,C}}{\rho_{M_yPc,o}} \right) \sum_{i=1}^{i=N_p} \left[w_{pi,o}(c_o - c_1)_i \left\{ 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \left(\frac{e^{-n^2\pi^2\bar{\tau}_{pi,o}}}{n^2} \right) \right\} \right], [coulomb] \quad (38)$$

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For the situation of $(c_o - c_1)$ being independent of the active material particle size distribution, i.e., $(c_o - c_1)_i = (c_o - c_1)$, Eqs. (36) and (38) lead to:

$$I^{t,C} = \left(\frac{6F\bar{D}m_o^{t,C}}{\rho_{M_yPc,o}} \right)(c_o - c_1)\left[\sum_{i=1}^{i=N_p} \left(\frac{w_{pi,o}}{a_{pi,o}^2} \right) \sum_{n=1}^{n=\infty} \exp\left(-n^2\pi^2\bar{\tau}_{pi,o}\right) \right], [A] \qquad (39)$$

$$\Delta Q^t = Q^t - Q_o^t = \left(\frac{Fm_o^{t,C}(c_o - c_1)}{\rho_{M_yPc,o}} \right)\sum_{i=1}^{i=N_p} w_{pi,o}\left\{ 1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left(\frac{e^{-n^2\pi^2\bar{\tau}_{pi,o}}}{n^2} \right) \right\}, [coulomb] \qquad (40)$$

Also, for the active material particles of only one size present in the cathode, Eqs. (39) and (40) lead to:

$$I^{t,C} = \left(\frac{6F\bar{D}m_o^{t,C}}{\rho_{M_yPc,o}} \right)\left(\frac{c_o - c_1}{a_{p,o}^2} \right)\sum_{n=1}^{n=\infty}\exp\left(-n^2\pi^2\tau_{p,o}\right), [A] \qquad (41)$$

$$\Delta Q^t = Q^t - Q_o^t = \left[\frac{Fm_o^{t,C}(c_o - c_1)}{\rho_{M_yPc,o}} \right]\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\left(\frac{e^{-n^2\pi^2\tau_{p,o}}}{n^2} \right) \right], [coulomb] \qquad (42)$$

where $\tau_{p,o} = \dfrac{\bar{D}t}{a_{p,o}^2}$.

It was experimentally shown [2] that the mass diffusivity of lithium in a metal phthalocyanine (e.g. FePc) cathode is a function of both the stored or intercalated lithium concentration and temperature. Therefore, the diffusivity of lithium in a M_yPc cathode particle is given by

$$D(x,T) = D_o(x)e^{-E_{a,D}/(RT)} \qquad (43)$$

where $D_o(x) =$ pre-exponential factor function of the stored lithium content,

$x = \left(\dfrac{\text{moles of the stored lithium}}{g\text{-}mole \text{ of the } M_yPc \text{ in the absence of stored lithium}} \right)$, $E_{a,D} =$ activation energy for lithium diffusion in M_yPc cathode active material particles; $R =$ universal gas content $= 8.314 J\ mol^{-1}K^{-1}$ and $T =$ absolute temperature $[K]$.

In Ref. [2] it has been shown that $D(x,T)$ at a temperature (for example, 20°C) decreases as x increases for lithium storage in the active material FePc particles. The mass diffusivity of lithium averaged over the stored-lithium in the cathode active material at any temperature is given by the following expression

$$\bar{D} = \left[\frac{\int_0^x D_o(x)\, dx}{x} \right] e^{-E_{a,D}/(RT)} \tag{44}$$

$$\bar{D} = \bar{D}_o \exp\left(\frac{-E_{a,D}}{RT} \right) \tag{45}$$

Under the assumption of the cell operation controlled by the solid-state diffusion of lithium in the cathode active material of M_yPc, the voltage loss associated with the lithium ion transport in the electrolyte and that associated with the electron transport in the acetylene black carbon may be assumed negligible. Simple estimates of these voltage losses, however, can be obtained from the following mathematical expressions at any time during the cell discharge period. Voltage loss associated with the ion transport in the electrolyte present in the composite cathode of thickness, l^C, can be estimated from:

$$\Delta\Phi^C_{electrolyte} = \frac{i_g^C l^C}{2\kappa^{C-electrolyte}_{eff-ion}} \tag{46}$$

where the effective ionic conductivity of the electrolyte in the cell cathode, $\kappa^{C-electrolyte}_{eff-ion}$, is given by

$$\kappa^{C-electrolyte}_{eff-ion} = \frac{\kappa^{C-electrolyte}_{ion} \varepsilon^{C-electrolyte}}{\tau^{C-electrolyte}} \tag{47}$$

In Eqs. (46) and (47), i_g^C = cathode electrode geometric current density $= \dfrac{I^{t,C}}{A_g^C}$, l^C = thickness of the cathode electrode, $\kappa^{C-electrolyte}_{ion}$ = ionic conductivity of the electrolyte, $\varepsilon^{C-electrolyte}$ = volume fraction of electrolyte in the cathode, and $\tau^{C-electrolyte}$ = tortuosity factor of the lithium ion-transport pathways in the electrolyte, $I^{t,C}$ = total current of the cell cathode, and A_g^C = cathode geometric area in contact with the cell electrolyte separator. The factor 2 in the denominator of Eq. (16a) appears because the ionic current in the electrolyte, at any time, at the cathode electrolyte-cathode current collector interface is zero and that at the cell separator-cathode interface is i_g^C. The voltage loss associated with the electron transport in the carbon black present in cathode can be estimated from

$$\Delta\Phi^{C-carbon}_{electron} = \frac{i_g^C l^C}{2\kappa^C_{eff-electronic}} \tag{48}$$

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where $\kappa^{C-carbon}_{eff-electronic}$ = effective electronic conductivity of cathode carbon and is given by

$$\kappa^{C-carbon}_{eff-electronic} = \frac{\kappa^{C-carbon}_{electronic}\, \varepsilon^{C-carbon}}{\tau^{C-carbon}} \tag{49}$$

where $\kappa^{C-carbon}_{electronic}$ = electronic conductivity of the carbon black present in the cell composite cathode, $\varepsilon^{C-carbon}$ = volume fraction of the carbon black in the cathode, and $\tau^{C-carbon}$ = tortuosity factor of the electron-transport pathways in the carbon black. It is here noted that the ratio of the Li_2Pc electronic conductivity [2] to that of the carbon black is of the order of $10^{-10}-10^{-11}$; indicating that the electronic transport in the cell cathode takes place mainly via the carbon black present in the cathode.

4.1.1.1 Reversible or Open-Circuit Potential of the Electrochemical Reaction at the Cell Cathode:

The electrochemical reaction that takes place at the boundary of three phases; a solid electronic conductor (e.g. carbon black), cathode active material (e.g. Li_xM_yPc), and an electrolyte (e.g. $LiBF_4$ in a microporous poly(ethylene oxide)); is represented as

$$\begin{bmatrix} Li^+_{\text{(in electrolyte)}} + e^-_{\text{(in carbon black)}} + \\ Li_xM_yPc_{\left(\begin{smallmatrix} x\ g\text{-}mole \text{ of the intercalated lithium} \\ \text{present in 1 }g\text{-}mole \text{ of initial }M_yPc \end{smallmatrix}\right)} \end{bmatrix} \Box \quad Li_{x+1}M_yPc_{\left(\begin{smallmatrix} (x+1)\ g\text{-}mole \text{ of the intercalated lithium} \\ \text{present in 1 }g\text{-}mole \text{ of initial }M_yPc \end{smallmatrix}\right)} \tag{50}$$

The intercalated lithium is treated as a solute present in solid-state solvent, e.g., M_yPc [5, 6, 7].

The thermodynamic equilibrium condition for the reaction (50) is

$$\begin{bmatrix} \mu^{echem}_{Li^+ \text{(in solid electrolyte)}} + \mu^{echem}_{e^- \text{(in solid carbon black)}} + \\ x\mu^{chem}_{Li \text{(in solid }M_yPc)} + \mu^{chem}_{M_yPc\text{(solid)}} \end{bmatrix} = (x+1)\,\mu^{chem}_{Li \text{(in solid }M_yPc)} + \mu^{chem}_{M_yPc\text{(solid)}} \tag{51}$$

Equation (51) leads to

$$\mu^{echem}_{Li^+ \text{(in solid electrolyte)}} + \mu^{echem}_{e^- \text{(in solid carbon black)}} = \mu^{chem}_{Li \text{(in solid }M_yPc)} \tag{52}$$

Expressing the species electrochemical potentials, μ^{echem}_i in Eq. (52), in terms of chemical and electrostatic potentials, leads to

$$\left[\mu^{chem}_{Li^+ \text{(in electrolyte)}} + z_{Li^+}F\Phi_{electrolyte} \right] + \left[\mu^{chem}_{e^- \text{(in carbon)}} + z_{e^-}F\Phi^C_{carbon} \right] = \mu^{chem}_{Li \text{(in }M_yPc)} \tag{53}$$

Simplification leads to:

$$F\left(\Phi_{electrolyte} - \Phi_{carbon}^{C}\right) = \left[\mu_{\text{Li(in M}_y\text{Pc})}^{chem} - \mu_{\text{Li}^+\text{(in electrolyte)}}^{chem} - \mu_{\text{e}^-\text{(in carbon)}}^{chem}\right] \tag{54}$$

Equation (54) is rewritten as

$$\left(\Phi_{carbon}^{C} - \Phi_{electrolyte}\right) = \left[\frac{\mu_{\text{Li}^+\text{(in electrolyte)}}^{chem} + \mu_{\text{e}^-\text{(in carbon)}}^{chem} - \mu_{\text{Li(in M}_y\text{Pc})}^{chem}}{F}\right] \tag{55}$$

where $\Phi_{electrolyte}$ = electrostatic potential in the electrolyte just outside of the double charge layer at the three phase, carbon black-cathode active material-electrolyte boundary and Φ_{carbon}^{C} = electrostatic potential in the carbon black electronic conductor in the cell cathode. By definition, $\left(\Phi_{carbon}^{C} - \Phi_{electrolyte}\right) = E_{rev}^{C}$ = reversible potential of the electrochemical reaction that occurs at the cell cathode for the cell open-circuit conditions. Now, Eq. (55) is written as

$$E_{rev}^{C} = \left[\frac{\mu_{\text{Li}^+\text{(in electrolyte)}}^{chem} + \mu_{\text{e}^-\text{(in carbon)}}^{chem} - \mu_{\text{Li(in M}_y\text{Pc})}^{chem}}{F}\right] \tag{56}$$

Expressing $\mu_{\text{Li}^+\text{(in electrolyte)}}^{chem}$ and $\mu_{\text{Li (in M}_y\text{Pc})}^{chem}$ as

$$\mu_{\text{Li}^+\text{(in electrolyte)}}^{chem} = \mu_{\text{Li}^+-\text{electrolyte}}^{o} + RT \ln a_{\text{Li}^+-\text{electrolyte}} \tag{57}$$

and

$$\mu_{\text{Li}-\text{M}_y\text{Pc}}^{chem} = \mu_{\text{Li}^+-\text{M}_y\text{Pc}}^{o} + RT \ln a_{\text{Li}-\text{M}_y\text{Pc}} \tag{58}$$

where $\mu_{\text{Li}^+-\text{electrolyte}}^{o}$ = standard-state chemical potential of Li^+ in the solid electrolyte, e.g., when $c_{\text{Li}^+-\text{electrolyte}}^{o} = 10^{-4} M$; $\mu_{\text{Li}-\text{M}_y\text{Pc}}^{o}$ = standard-state chemical potential of lithium in the cathode active material, e.g., when the intercalated lithium concentration, $c_{\text{Li}-\text{M}_y\text{Pc}}^{o} = x^o c_{\text{M}_y\text{Pc},o}$, where $x^o = 10^{-9}$ g-$mole$ of the intercalated lithium per g-$mole$ of M_yPc and $c_{\text{M}_y\text{Pc},o}$ = initial molar concentration of the cathode active material M_yPc; the activity of Li^+ in the electrolyte,

$a_{\text{Li}^+-\text{electrolyte}} = \gamma_{\text{Li}^+-\text{electrolyte}} \dfrac{c_{\text{Li}^+-\text{electrolyte}}}{c_{\text{Li}^+-\text{electrolyte}}^{o}}$; and the activity of lithium in M_yPc,

$a_{\text{Li}-\text{M}_y\text{Pc}} = \gamma_{\text{Li}-\text{M}_y\text{Pc}} \dfrac{c_{\text{Li}-\text{M}_y\text{Pc}}}{c_{\text{Li}-\text{M}_y\text{Pc}}^{o}} = \gamma_{\text{Li}-\text{M}_y\text{Pc}} \left(\dfrac{xc_{\text{M}_y\text{Pc},o}}{x^o c_{\text{M}_y\text{Pc},o}}\right) = \gamma_{\text{Li}-\text{M}_y\text{Pc}} \left(\dfrac{x}{x^o}\right).$

Inserting the information from Eqs. (57) and (58) into Eq. (56) leads to

$$E_{rev}^{C} = \left(\frac{\mu_{\text{Li}^+-\text{electrolyte}}^{o} + \mu_{\text{e}^--\text{carbon}}^{o} - \mu_{\text{Li}-\text{M}_y\text{Pc}}^{o}}{F} \right) + \left(\frac{RT}{F} \right) \ln \left(\frac{a_{\text{Li}^+-\text{electrolyte}}}{a_{\text{Li}-\text{M}_y\text{Pc}}} \right) \tag{59}$$

Note that in obtaining of Eq. (59), the actual state of a charge conducting electron in carbon has been taken to be equal to its standard state. Equation (59) is rewritten as

$$E_{rev}^{C} = E^{C,o} + \left(\frac{RT}{F} \right) \ln \left(\frac{\gamma_{\text{Li}^+-\text{electrolyte}} \left(\dfrac{c_{\text{Li}^+-\text{electrolyte}}}{c_{\text{Li}^+-\text{electrolyte}}^{o}} \right)}{\gamma_{\text{Li}-\text{M}_y\text{Pc}} \left(\dfrac{x}{x^o} \right)} \right) \tag{60}$$

where the standard-state electric potential of the reaction that occurs at the cathode, $E^{C,o}$ is given as

$$E^{C,o} = \left(\frac{\mu_{\text{Li}^+-\text{electrolyte}}^{o} + \mu_{\text{e}^--\text{carbon}}^{o} - \mu_{\text{Li}-\text{M}_y\text{Pc}}^{o}}{F} \right) \tag{61}$$

Equation (60) is re-written as

$$E_{rev}^{C} = E^{C,o} + \left(\frac{RT}{F} \right) \ln \left\{ \gamma_{\text{Li}^+-\text{electrolyte}} \left(\frac{c_{\text{Li}^+-\text{electrolyte}}}{c_{\text{Li}^+-\text{electrolyte}}^{o}} \right) \right\} - \left(\frac{RT}{F} \right) \ln \left\{ \gamma_{\text{Li}-\text{M}_y\text{Pc}} \left(\frac{x}{x^o} \right) \right\} \tag{62}$$

Equation (62) can be written as:

$$E_{rev}^{C} = E^{C,o} + \left(\frac{RT}{F} \right) \left[\ln \left(\frac{\gamma_{\text{Li}^+-\text{electrolyte}} c_{\text{Li}^+-\text{electrolyte}}}{c_{\text{Li}^+-\text{electrolyte}}^{o}} \right) - \ln \left(\frac{\gamma_{\text{Li}-\text{M}_y\text{Pc}}}{x^o} \right) \right] - \left(\frac{RT}{F} \right) \ln x \tag{63}$$

$$E_{rev}^{C} = E_G^{C,o} - \left(\frac{RT}{F} \right) \ln x \tag{64}$$

where

$$E_G^{C,o} = E^{C,o} + \left(\frac{RT}{F} \right) \ln \left(\frac{\gamma_{\text{Li}^+-\text{electrolyte}}}{\gamma_{\text{Li}-\text{M}_y\text{Pc}}} \cdot \frac{c_{\text{Li}^+-\text{electrolyte}}}{c_{\text{Li}^+-\text{electrolyte}}^{o}} \cdot x^o \right) \tag{65}$$

For a given electrolyte at a temperature, $E_G^{C,o}$ would be constant with respect to x if variation in $\gamma_{\text{Li}-\text{M}_y\text{Pc}}$ is assumed to be negligibly small. Equation (64) suggests that E_{rev}^C has a linear relation with $\ln x$; provided $\gamma_{\text{Li}-\text{M}_y\text{Pc}}$ is constant with respect to x. So, the plot of measured values of E_{rev}^C vs. $\ln x$ should turn out to be a straight line with $\text{slope} = \left(\dfrac{-RT}{F} \right)$. If so, then, one can determine $E_G^{C,o}$ from the measured values of E_{rev}^C vs. x using Eq. (64). Finally, the relation, Eq. (64), can be employed to compute E_{rev}^C as a function of x for the prediction of performance of a lithium-ion cell.

Equation (62) can also be expressed as

$$E_{rev}^C = E^{C,o} + \left(\frac{RT}{F} \right) \ln \left(\frac{\gamma_{\text{Li}^+ - \text{electrolyte}}}{\gamma_{\text{Li}-\text{M}_y\text{Pc}}} \right) - \left(\frac{RT}{F} \right) \ln \left(\frac{c_{\text{Li}^+ - \text{electrolyte}}^o}{c_{\text{Li}^+ - \text{electrolyte}}} \right) - \left(\frac{RT}{F} \right) \ln \left(\frac{x}{x^o} \right) \qquad (66)$$

For the assumption of $\left(\dfrac{\gamma_{\text{Li}^+ - \text{electrolyte}}}{\gamma_{\text{Li}-\text{M}_y\text{Pc}}} \right) = \text{constant}$, Eq. (66) suggests that E_{rev}^C decreases as x increases above x^o for a fixed $c_{\text{Li}^+ - \text{electrolyte}}$; whereas E_{rev}^C increases as $c_{\text{Li}^+ - \text{electrolyte}}$ increases above $c_{\text{Li}^+ - \text{electrolyte}}^o$ for a fixed x value at a temperature.

4.1.1.2 Electrode Kinetics at the Cell Cathode:

The cathode electrochemical reaction takes place at the boundary of three phases − a solid electronic conductor (carbon black), cathode active material and an electrolyte. The electrochemical reaction is represented as

$$\text{Li}^+_{(\text{in electrolyte})} + e^-_{(\text{in carbon black})} + \text{M}_y\text{Pc} \underset{k_b^{C,1}}{\overset{k_f^{C,1}}{\rightleftharpoons}} \text{Li}_{\left(\substack{\text{in } 1g\text{-}mole \text{ of the solid-} \\ \text{state solvent of M}_y\text{Pc}} \right)} \qquad (67)$$
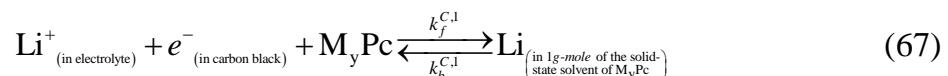
It is here assumed that the cathode active material, M_yPc, is a solid-state solvent for lithium storage of the intercalated lithium during the period of cell discharge. The forward or cathodic direction process of the reaction, Eq. (67), which has units of $\left[\dfrac{g - mols \text{ of the forward reaction process}}{\text{time} \,\square\, \text{active material interfacial area}} \right]$, is simulated by

$$r_f^C = k_f^{C,1} a_{\text{Li}^+ - \text{in electrolyte}} a_{\text{M}_y\text{Pc}} e^{-\beta^C E^C F/(RT)} \qquad (68)$$

where $\beta^C = $ symmetry factor; indicative of the fraction of the voltage difference, E^C, (difference between the electrostatic potentials at the three-phase boundary and in the electrolyte just outside the double charge layer) involved in the cathodic direction charge transfer process;

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$a_{\text{Li}^+-\text{in electrolyte}}$ = activity of lithium ions in the electrolyte = $\gamma_{\text{Li}^+,\text{conc}}\left(\dfrac{c_{\text{Li}^+}}{c^o_{\text{Li}^+}}\right)$ (dimensionless),

$\gamma_{\text{Li}^+,\text{conc}}$ = activity coefficient of lithium ions in the polymer electrolyte, c_{Li^+} = molar concentration of lithium ions in the electrolyte, $c^o_{\text{Li}^+}$ = molar concentration of Li^+ in the polymer electrolyte when the electrolyte active component, e.g., LiBF_4 is present in 'infinitely' dilute form, e.g., $c^o_{\text{Li}^+} = 10^{-4} M$, taken to be the standard state of Li^+ in the electrolyte at which state $\gamma_{\text{Li}^+,\text{conc}} = 1$ and $a_{\text{Li}^+-\text{in electrolyte}} = 1$; $a_{\text{M}_y\text{Pc}}$ = activity of the cathode active material, M_yPc, here $a_{\text{M}_y\text{Pc}}$ may be taken equal to 1 because M_yPc is assumed to be a solid solvent for lithium storage; F = Faraday's constant = 96487 coulomb of charge per *g*-equivalent or *g-mole* of 'unitly' charged particles (e.g., electron, lithium ion); R = gas constant = 8.314 $J\ mol^{-1}\ K^{-1}$; T = temperature at the three-phase boundary, [K]; and $k^{C,1}_f$ = rate coefficient for the forward or cathodic direction process of the reaction, Eq. (67), $\left[\dfrac{g\text{-}mole}{cm^2\cdot\sec}\right]$. The rate equation (68) is rewritten as

$$r^C_f = \left(k^{C,1}_f a_{\text{M}_y\text{Pc}}\gamma_{\text{Li}^+,\text{conc}}\right)\left(\frac{c_{\text{Li}^+}}{c^o_{\text{Li}^+}}\right)e^{-\beta^C E^C F/(RT)} \tag{69}$$

$$= k^C_f\left(\frac{c_{\text{Li}^+}}{c^o_{\text{Li}^+}}\right)e^{-\beta^C E^C F/(RT)} \tag{70}$$

where

$$k^C_f = \left(k^{C,1}_f a_{\text{M}_y\text{Pc}}\gamma_{\text{Li}^+,\text{conc}}\right), \left[\frac{g\text{-}mol}{cm^2\text{-}\sec}\right] \tag{71}$$

The rate of the anodic, oxidation direction process of the reaction, Eq. (67), is assumed to be dependent on the intercalated lithium activity in the cathode active material M_yPc. The anodic direction reaction process, with units of $\left[\dfrac{g\text{-}moles \text{ of the anodic direction reaction process occuring}}{cm^2\cdot\sec}\right]$, is represented by

$$r^C_b = k^{C,1}_b a_{\text{Li-in M}_y\text{Pc}} e^{\frac{(1-\beta^C)E^C F}{RT}} \tag{72}$$

where $\left(1-\beta^C\right)$ = fraction of the voltage difference, E^C, involved in the anodic direction charge transfer process; $a_{\text{Li-in M}_y\text{Pc}}$ = activity of lithium intercalated in the active material M_yPc

$$= \gamma_{\text{Li, conc}}^{C} \frac{c_{\text{Li-in M}_y\text{Pc}}^{C}}{c_{\text{Li-in M}_y\text{Pc}}^{o}} = \gamma_{\text{Li, conc}}^{C} \frac{x c_{\text{M}_y\text{Pc}}}{x^o c_{\text{M}_y\text{Pc}}} = \gamma_{\text{Li, conc}}^{C} \left(\frac{x}{x^o}\right), \quad \gamma_{\text{Li, conc}}^{C} = \text{activity coefficient of lithium in the}$$

cathode active material, M_yPc, $c_{\text{Li-in M}_y\text{Pc}} = $ molar concentration of the intercalated lithium in M_yPc, $c_{\text{Li-in M}_y\text{Pc}}^{o} = $ molar concentration of lithium in M_yPc when it is present in M_yPc in the 'infinitely' dilute form, e.g., $x^o = 10^{-9}$, for which state $a_{\text{Li-in M}_y\text{Pc}} = 1$, $\gamma_{\text{Li, conc}} = 1$, $x = g\text{-mole}$ of the intercalated lithium per $g\text{-mole}$ of M_yPc; $k_b^{C,1} = $ reaction rate coefficient for the anodic direction charge transfer process. Equation (72) is rewritten as

$$r_b^C = \left(k_b^{C,1} \gamma_{\text{Li, conc}}^{C}\right) \left(\frac{x}{x^o}\right) e^{\frac{\left(1-\beta^C\right)E^C F}{RT}} \tag{73}$$

$$r_b^C = k_b^C \left(\frac{x}{x^o}\right) e^{\frac{\left(1-\beta^C\right)E^C F}{RT}} \tag{74}$$

where,

$$k_b^C = \left(k_b^{C,1} \gamma_{\text{Li, conc}}^{C}\right), \left[\frac{g\text{-mole}}{cm^2\text{-sec}}\right] \tag{75}$$

is the rate coefficient for the backward or anodic direction charge transfer process.

The net reaction rate at the cathode during the period of lithium intercalation into the cathode active material, i.e., during the cell discharge period, is given by

$$\left|r^C\right| = r_f^C - r_b^C = \left[k_f^C \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}^+}^{o}}\right) e^{\frac{-\beta^C E^C F}{RT}} - k_b^C \left(\frac{x}{x^o}\right) e^{\frac{\left(1-\beta^C\right)E^C F}{RT}}\right] \tag{76}$$

Because $c_{\text{Li}^+}^{o}$ and x^o are constants for the selected standard states, Eq. (76) is transformed to:

$$\left|r^C\right| = \left[k_{ff}^C c_{\text{Li}^+} e^{\frac{-\beta^C E^C F}{RT}} - k_{bb}^C x e^{\frac{\left(1-\beta^C\right)E^C F}{RT}}\right] \tag{77}$$

where $k_{ff}^C = \left(\frac{k_f^C}{c_{\text{Li}^+}^{o}}\right), \left[\frac{cm}{\text{sec}}\right]$ and $k_{bb}^C = \left(\frac{k_b^C}{x^o}\right), \left[\frac{g\text{-mol}}{cm^2 \cdot \text{sec}}\right]$.

The net reaction rate, $\left|r^C\right|$, is related to the interfacial charge transfer current density, $\left|i_s^C\right|$, at the cathode by the following equation:

$$\frac{\left|i_s^C\right|}{F} = \frac{\left|r^C\right|}{1} = \left[k_{ff}^C c_{Li^+} e^{\frac{-\beta^C E^C F}{RT}} - k_{bb}^C x e^{\frac{\left(1-\beta^C\right)E^C F}{RT}} \right] \qquad (78)$$

Or,

$$\frac{\left|i_s^C\right|}{F} = \left|r^C\right| = k_{ff}^C \left[c_{Li^+} e^{\frac{-\beta^C E^C F}{RT}} - \frac{x e^{\frac{\left(1-\beta^C\right)E^C F}{RT}}}{K^C} \right] \qquad (79)$$

where $K^C = \dfrac{k_{ff}^C}{k_{bb}^C}, \left[g\text{-}mole\ cm^{-3}\right]^{-1}$ is the kinetics based equilibrium constant for the reaction at the cell cathode.

For the reaction equilibrium at the cathode, $\left|i_s^C\right| = 0$, where

$$E^C = E_{rev}^C \qquad (80)$$

Using Eq. (79) in Eq. (80) and simplification leads to

$$F c_{Li^+}^{eq} e^{\frac{-\beta^C E_{rev}^C F}{RT}} = \frac{F x^{eq} e^{\frac{\left(1-\beta^C\right)E_{rev}^C F}{RT}}}{K^C} \qquad (81)$$

where x^{eq} is the number of *g-moles* of the intercalated lithium per *g-mole* of the cathode active material, M_yPc, for the equilibrium between the electrolyte and the active material with respect to lithium.

Equation (81) is re-expressed as

$$F k_{ff}^C c_{Li^+}^{eq} e^{\frac{-\beta^C E_{rev}^C F}{RT}} = F k_{bb}^C x^{eq} e^{\frac{\left(1-\beta^C\right)E_{rev}^C F}{RT}} = i_o^C \qquad (82)$$

where $i_o^C =$ exchange current density, $\left[A \cdot cm_{interface}^{-2}\right]$ and $E_{rev}^C =$ potential difference between the electrostatic potential in the electronic conductor at the three-phase boundary and that in the electrolyte just outside the double-charge layer at the equilibrium state.

Determination of E^C and E_{rev}^C is, in general, difficult. So, it is here suggested that E^C and E_{rev}^C may be measured relative to a reference electrode. The surface overpotential at the three phase boundary of the cell cathode, due to a finite value of $\left|i_s^C\right|$, is defined as

$$\eta_s^C = E^C - E_{rev}^C \tag{83}$$

The surface overpotential, η_s^C, is also called the activation polarization voltage change associated with the electrochemical reaction involving the charge transfer process across the cathode three phase boundary. Substituting $E^C = E_{rev}^C + \eta_s^C$ in Eq. (78) leads to

$$\left| i_s^C \right| = \left[k_{ff}^C F c_{Li^+} e^{\frac{-\beta^C E_{rev}^C F}{RT}} e^{\frac{-\beta^C \eta_s^C F}{RT}} - k_{bb}^C F x e^{\frac{(1-\beta^C) E_{rev}^C F}{RT}} e^{\frac{(1-\beta^C)\eta_s^C F}{RT}} \right] \tag{84}$$

$$\left| i_s^C \right| = i_o^C \left[\left(\frac{c_{Li^+}}{c_{Li^+}^{eq}} \right) e^{\frac{-\beta^C \eta_s^C F}{RT}} - \left(\frac{x}{x^{eq}} \right) e^{\frac{(1-\beta^C)\eta_s^C F}{RT}} \right] \tag{85}$$

The cathodic charge transfer coefficient, α_c^C, and the anodic charge transfer coefficient, α_a^C, are defined as follows: $\alpha_c^C = \beta^C n = \beta^C; \alpha_a^C = (1-\beta^C)n = 1-\beta^C$; because for the electrochemical reaction at the cell cathode, Eq. (67), n, the number of electrons transferred per one reaction-event is equal to 1.

The expression for the current density at the cathode three phase boundary from Eq. (85) is now written as

$$\left| i_s^C \right| = i_o^C \left[\left(\frac{c_{Li^+}}{c_{Li^+}^{eq}} \right) e^{\frac{-\alpha_c^C \eta_s^C F}{RT}} - \left(\frac{x}{x^{eq}} \right) e^{\frac{\alpha_a^C \eta_s^C F}{RT}} \right] \tag{86}$$

Equation (86) suggests that as x increases during the cell discharge period, the current density should decrease. When the intercalated lithium in the cathode material attains a value of $x = x^{eq}$, $\eta_s^C = 0$, and $c_{Li^+} = c_{Li^+}^{eq}$; $\left| i_s^C \right|$ becomes equal to zero.

Equation (82) is used to obtain the following equation

$$e^{\left(\frac{E_{rev}^C F}{RT} \right)} = \frac{k_{ff}^C c_{Li^+}^{eq}}{k_{bb}^C x^{eq}} \tag{87}$$

Taking $\log_e$ of both sides of Eq. (87) leads to

$$E_{rev}^C = \left[\left(\frac{RT}{F} \right) \ln \left(\frac{k_{ff}^C c_{Li^+}^{eq}}{k_{bb}^C} \right) - \left(\frac{RT}{F} \right) \ln x^{eq} \right] \tag{88}$$

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Or, $E_{rev}^C = \left(\dfrac{RT}{F}\right)\ln\left(\dfrac{k_{ff}^C}{k_{bb}^C}\right) + \left(\dfrac{RT}{F}\right)\ln\left(\dfrac{c_{\text{Li}^+}^{eq}}{x^{eq}}\right)$

Equation (88) is the desired formula to compute E_{rev}^C based on the kinetics of the electrochemical reaction that occurs at the cell cathode. Note that Eq. (88) is similar to Eq. (64) derived using the thermodynamic principle of reaction equilibrium to compute the reaction equilibrium electric potential at the cathode active material−electrolyte interface for a given electrolyte and cathode active material, such as M_yPc at a cathode temperature.

If one knows the experimental values of E_{rev}^C and x^{eq}, one can determine $\left(\dfrac{k_{ff}^C}{k_{bb}^C}\right)$ for a given electrolyte from Eq. (88). Inserting the information given in Eq. (87) into Eq. (82) leads to

$$i_o^C = F\left(k_{bb}^C x^{eq}\right)^{\beta^C}\left(k_{ff}^C c_{\text{Li}^+}^{eq}\right)^{\left(1-\beta^C\right)} \tag{89}$$

Notice the relation of the exchange current density, i_o^C, with the chemical and electrochemical kinetic parameters without the involvement of the reversible electrochemical reaction potential, E_{rev}^C, at the cell cathode.

From Eq. (86), with $c_{\text{Li}^+} = c_{\text{Li}^+}^{eq}$, particularly for the situation of the lithium diffusion in the cathode active material particles controlling the overall cell performance, one obtains:

$$\left|i_s^C\right| = i_o^C\left[1-\left(\frac{x}{x^{eq}}\right)e^{\frac{\left(\alpha_a^C+\alpha_c^C\right)\eta_s^C F}{RT}}\right]e^{\frac{-\alpha_c^C\eta_s^C F}{RT}} \tag{90}$$

Taking $\log_e$ of both sides of Eq. (90) and further simplification leads to

$$\ln\left[\frac{\left|i_s^C\right|}{1-\left(\dfrac{x}{x^{eq}}\right)\exp\left(\dfrac{\left(\alpha_a^C+\alpha_c^C\right)\eta_s^C F}{RT}\right)}\right] = \ln i_o^C + \frac{\alpha_c^C F}{RT}\left(-\eta_s^C\right) \tag{91}$$

One should note that $\left(\alpha_a^C+\alpha_c^C\right)=\left(1-\beta^C\right)n+\beta^C n = n = 1$ for the electrochemical reaction, Eq. (67).

Equation (91) suggests that $\ln\left[\dfrac{\left|i_s^C\right|}{1-\left(\dfrac{x}{x^{eq}}\right)\exp\left(\dfrac{\left(\alpha_a^C+\alpha_c^C\right)\eta_s^C F}{RT}\right)}\right]$ plotted versus $\left(-\eta_s^C\right)$ should

be a straight line with slope $=\left(\dfrac{\alpha_c^C F}{RT}\right)$ and intercept $=\ln i_o^C$, provided i_o^C does not vary as

$\left(-\eta_s^C\right)$ is varied.

Such a plot based on the experimental data of $\left|i_s^C\right|$, x, x^{eq}, and $\left(-\eta_s^C\right)$ should be used to obtain electrokinetic parameters $\alpha_c^C\left(=\beta^C n\right)$ and i_o^C, the exchange current density for the electrochemical reaction, Eq. (67).

For the low surface overpotential, $\left(-\eta_s^C\right)$; i.e., for a low value of $\left|i_s^C\right|$, the Taylor series

expansion of $e^{\frac{-\alpha_c^C \eta_s^C F}{RT}}$ and $e^{\frac{\alpha_a^C \eta_s^C F}{RT}}$ in Eq. (86) leads to

$$\left|i_s^C\right|=i_o^C\left[\left(1-\frac{x}{x^{eq}}\right)+\left(\alpha_c^C+\alpha_a^C\left(\frac{x}{x^{eq}}\right)\right)\frac{F}{RT}\left(-\eta_s^C\right)\right] \tag{92}$$

For the cathode active material composition state close to that in equilibrium with the electrolyte, i.e., for $x\cong x^{eq}$, Eq. (92) leads to

$$\left|i_s^C\right|=i_o^C\left(\alpha_c^C+\alpha_a^C\right)\frac{F}{RT}\left(-\eta_s^C\right)=i_o^C\left(\frac{F}{RT}\right)\left(-\eta_s^C\right) \tag{93}$$

This equation suggests that the experimental data on $\left|i_s^C\right|$ obtained as a function of $\left(-\eta_s^C\right)$ for low values of $\left(-\eta_s^C\right)$, with the cathode active material composition state close to its state in equilibrium with the electrolyte, can be employed to obtain i_o^C experimentally.

For $\left(\alpha_c^C\left(-\eta_s^C\right)F\right)\gg RT$, Eq. (86) reduces to

$$\left|i_s^C\right|=i_o^C e^{\frac{-\alpha_c^C \eta_s^C F}{RT}} \tag{94}$$

Or,

$$\eta_s^C=\left(-\frac{RT}{\alpha_c^C F}\right)\ln\left(\frac{\left|i_s^C\right|}{i_o^C}\right) \tag{95}$$

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For $\alpha_a^C \eta_s^C F \gg RT$, Eq. (86) reduces to

$$i_s^C = -i_o^C \left(\frac{x}{x^{eq}} \right) e^{\frac{\alpha_a^C \eta_s^C F}{RT}} \qquad (96)$$

Or,

$$\ln\left(\frac{-i_s^C}{i_o^C} \right) = \ln\left(\frac{x}{x^{eq}} \right) + \left(\frac{\alpha_a^C F}{RT} \right) \eta_s^C \qquad (97)$$

Equation (97) leads to

$$\eta_s^C = \left(\frac{RT}{\alpha_a^C F} \right) \ln\left[\frac{\left| -i_s^C \right|}{i_o^C} \left(\frac{x^{eq}}{x} \right) \right] \qquad (98)$$

Plot of η_s^C vs. $\ln\left(\dfrac{i_s^C}{i_o^C} \right)$ or plot of η_s^C vs. $\ln\left[\dfrac{\left| -i_s^C \right|}{i_o^C} \left(\dfrac{x^{eq}}{x} \right) \right]$ is called the Tafel plot. The Tafel

slope is either $\left(\dfrac{-RT}{\alpha_c^C F} \right)$ or $\left(\dfrac{RT}{\alpha_a^C F} \right)$.

4.1.2 Electrolyte Separator Formulation

The geometric current flow density through the electrolyte separator of microporous poly(ethylene oxide) containing LiBF$_4$ is computed from

$$i_g^S = \frac{I^{t,C}}{A_g^S} \qquad (99)$$

where A_g^S = geometric area of the separator perpendicular to the current flow direction. For the situation of the lithium-ion cell performance controlled by the diffusion of intercalating lithium in the cathode active material, the lithium ion concentration gradient in the polymer separator is assumed to be negligible. The voltage loss in the electrolyte separator is given by

$$\Delta\Phi_{electrolyte}^S = \frac{i_g^S l^S}{\kappa_{eff}^{S-electrolyte}} \qquad (100)$$

where l^S = thickness of the electrolyte separator and $\kappa_{eff}^{S-electrolyte}$ = ionic conductivity of LiBF$_4$ in microporous poly(ethylene oxide).

4.1.3   Anode Formulation

4.1.3.1   Electrode Kinetics at the Cell Anode

For the anode of a thin lithium sheet in contact with the electrolyte separator, the electrochemical reaction occurring at the anode-electrolyte interface is represented as

$$\text{Li}(s) \underset{k_b^{A,1}}{\overset{k_f^{A,1}}{\rightleftharpoons}} \text{Li}^+ \left(\text{in electrolyte}\right) + e^- \left(\text{in metal of Li}\right) \tag{101}$$
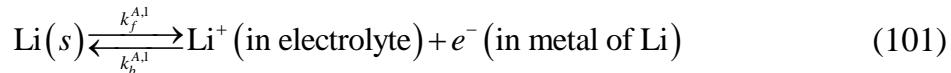
The forward reaction rate of the electrochemical reaction, Eq. (101), which has units of $\left[\dfrac{g\text{-}mole}{\text{sec} \cdot cm^2 \text{ interface}}\right]$, is expressed as

$$r_f^A = k_f^{A,1} a_{\text{Li}(s)} e^{\left(1-\beta^A\right)E^A F/RT} = k_f^{A,1} e^{\left(1-\beta^A\right)E^A F/RT} \tag{102}$$

where $k_f^{A,1}$ = forward reaction rate coefficient, $\left[\dfrac{g\text{-}mole}{\text{sec} \cdot cm^2 \text{ interface}}\right]$, $a_{\text{Li}(s)}$ = activity of solid-state lithium=1 (a usual assumption), β^A = symmetry factor for the electrochemical reaction, Eq. (22a), E^A = difference between the electrostatic potential in metal of lithium and that in the electrolyte just outside the double-charge layer at the cell anode-electrolyte interface, $\left[V\right]$, when, for example, the cell is being discharged.

The backward direction reaction rate of the reaction, Eq. (101), which has units of $\left[\dfrac{g\text{-}mole}{\text{sec} \cdot cm^2 \text{ interface}}\right]$, is represented as:

$$r_b^A = k_b^{A,1} a_{\text{Li}^+(\text{in electrolyte})} e^{-\beta^A E^A F/RT} \tag{103}$$

where $k_b^{A,1}$ = the backward direction reaction-rate coefficient for the reversible reaction, Eq. (101), $\left[\dfrac{g\text{-}moles}{\text{sec} \cdot cm^2 \text{ interface}}\right]$, $a_{\text{Li}^+(\text{in electrolyte})} = \gamma_{\text{Li}^+} \dfrac{c_{\text{Li}^+}}{c_{\text{Li}^+}^o}$ = activity of Li$^+$ in the electrolyte solution adjacent to the anode electrode-electrolyte interface just outside the double-charge layer, c_{Li^+} = molar concentration of Li$^+$ in the electrolyte solution adjacent to the electrode-electrolyte interface, and $c_{\text{Li}^+}^o$ = standard-state concentration of Li$^+$ when it is present in 'infinitely dilute form' in the solvent, here, poly(ethylene oxide), γ_{Li^+} = activity coefficient of lithium ions in the

electrolyte to account for the non-ideal behavior of Li^+ in the solvent. For Li^+ ions present in an 'infinity dilute form' in the electrolyte, e.g., $c^o_{Li^+} = 10^{-4}M$, $\gamma_{Li^+} = \gamma^\infty_{Li^+} = 1$ and $a^\infty_{Li^+} = 1$.

Equation (103) is rewritten as

$$r^A_b = \left(k^{A,1}_b \gamma_{Li^+}\right)\left(\frac{c_{Li^+}}{c^o_{Li^+}}\right)e^{-\beta^A E^A F/RT} \tag{104}$$

$$r^A_b = k^A_b \left(\frac{c_{Li^+}}{c^o_{Li^+}}\right)e^{-\beta^A E^A F/RT} \tag{105}$$

where

$$k^A_b = \left(k^{A,1}_b \gamma_{Li^+}\right) \tag{106}$$

and has units of $\left[\dfrac{g\text{-}mole}{sec \cdot cm^2 \text{ interface}}\right]$.

The reaction rate expressions, Eqs. (102) and (104), are now represented as

$$r^A_f = k^A_{ff} e^{(1-\beta^A)E^A F/RT} \tag{107}$$

$$r^A_b = k^A_{bb} c_{Li^+} e^{-\beta^A E^A F/RT} \tag{108}$$

where

$$k^A_{ff} = k^{A,1}_f, \left[\frac{g\text{-}mole}{sec \cdot cm^2 \text{ interface}}\right] \tag{109}$$

$$k^A_{bb} = \left(\frac{k^{A,1}_b \gamma_{Li^+}}{c^o_{Li^+}}\right), \left[\frac{cm}{sec}\right] \tag{110}$$

The net reaction rate at the anode during the cell discharge period, which has units of $\left[\dfrac{g\text{-}moles \text{ of reaction (101) occuring}}{sec \cdot cm^2 \text{ interface}}\right]$, is given by

$$\frac{\left|i^A_s\right|}{F} = \left|r^A\right| = r^A_f - r^A_b = k^A_{ff} e^{(1-\beta^A)E^A F/RT} - k^A_{bb} e^{-\beta^A E^A F/RT} c_{Li^+} \tag{111}$$

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where $\left|i_s^A\right|$ = interfacial charge-transfer current density, $\left[\dfrac{A}{cm^2}\right]$ during the period of cell discharge.

For the reaction, Eq. (101), to be at equilibrium;

$$\left|i_s^A\right| = 0 \tag{112}$$

Using the result from Eq. (111) in Eq. (112) leads to

$$Fk_{ff}^A e^{\left(1-\beta^A\right)E_{rev}^A F/RT} = Fk_{bb}^A e^{-\beta^A E_{rev}^A F/RT} c_{Li^+}^{eq} = i_o^A \tag{113}$$

where i_o^A = exchange current density for the electrochemical reaction, Eq. (101); and E_{rev}^A = difference between the electrostatic potential in the anode electrode and the electrostatic potential in the electrolyte adjacent to the electrode-electrolyte interface for the anodic reaction, Eq. (101), to be at equilibrium.

The surface overpotential, with units of volts, at the electrode-electrolyte interface, η_s^A, is defined as

$$\eta_s^A = E^A - E_{rev}^A \tag{114}$$

The surface overpotential, η_s^A, is also called the activation polarization voltage change associated with the electrochemical reaction, Eq. (101), involving the charge transfer process across the electrolyte-anode electrode interface. Inserting $E^A = \left(E_{rev}^A + \eta_s^A\right)$ into Eq. (111) leads to

$$\left|i_s^A\right| = \left[k_{ff}^A Fe^{\frac{\left(1-\beta^A\right)FE_{rev}^A}{RT}} e^{\frac{\left(1-\beta^A\right)F\eta_s^A}{RT}} - k_{bb}^A Fc_{Li^+} e^{\frac{-\beta^A FE_{rev}^A}{RT}} e^{\frac{-\beta^A F\eta_s^A}{RT}}\right] \tag{115}$$

Using the information from Eq. (113) in Eq. (115) leads to

$$\left|i_s^A\right| = i_o^A \left[e^{\frac{\left(1-\beta^A\right)\eta_s^A F}{RT}} - \left(\frac{c_{Li^+}}{c_{Li^+}^{eq}}\right)e^{\frac{-\beta^A \eta_s^A F}{RT}}\right], \left[\frac{A}{cm_{surf}^2}\right] \tag{116}$$

Note that $\eta_s^A = E^A - E_{rev}^A$ is a positive number quantity during the period the cell is providing electric power to an external circuit.

From Eq. (113), one finds that

$$e^{\frac{E_{rev}^{A}F}{RT}} = \left(\frac{k_{bb}^{A}c_{\text{Li}^+}^{eq}}{k_{ff}^{A}} \right) \tag{117}$$

Take $\log_e$ of both sides of Eq. (117) to obtain

$$E_{rev}^{A} = \left(\frac{RT}{F} \right) \ln \left(\frac{k_b^{A,1}\gamma_{\text{Li}^+}}{k_{ff}^{A}} \right) + \left(\frac{RT}{F} \right) \ln \left(\frac{c_{\text{Li}^+}^{eq}}{c_{\text{Li}^+}^{o}} \right) \tag{118}$$

Or,

$$E_{rev}^{A} = E^{A,o'} + \left(\frac{RT}{F} \right) \ln \left(\frac{c_{\text{Li}^+}^{eq}}{c_{\text{Li}^+}^{o}} \right) \tag{119}$$

where $E^{A,o'} = \left(\dfrac{RT}{F} \right) \ln \left(\dfrac{k_b^{A,1}\gamma_{\text{Li}^+}}{k_{ff}^{A}} \right)$.

Or,

$$E_{rev}^{A} = E_{kinet}^{A,o} + \left(\frac{RT}{F} \right) \ln \left(\frac{\gamma_{\text{Li}^+}c_{\text{Li}^+}^{eq}}{c_{\text{Li}^+}^{o}} \right) \tag{120}$$

where $E_{kinet}^{A,o} = \left(\dfrac{RT}{F} \right) \ln \left(\dfrac{k_b^{A,1}}{k_{ff}^{A}} \right)$.

Equation (119) is the kinetics based expression to compute the anode reaction reversible electric potential or the cell open-circuit anode electrode potential. At the cell open-circuit condition, $c_{\text{Li}^+}^{eq} \cong c_{\text{Li}^+}$, lithium-ion concentration in the bulk electrolyte. Note that $E_{rev}^{A} = E^{A,o} =$ standard-state electric potential of the electrochemical reaction, Eq. (101), for $c_{\text{Li}^+}^{eq} = c_{\text{Li}^+} = c_{\text{Li}^+}^{o}$.

Equation (119) tells us that as $\left(\dfrac{c_{\text{Li}^+}^{eq}}{c_{\text{Li}^+}^{o}} \right) = \left(\dfrac{c_{\text{Li}^+}}{c_{\text{Li}^+}^{o}} \right)$ is increased, the anode electrode reversible electric potential increases.

Using the information from Eq. (117) in Eq. (113) leads to

$$i_A^o = F \left(k_{ff}^{A} \right)^{\beta^A} \left(k_{bb}^{A}c_{\text{Li}^+}^{eq} \right)^{\left(1-\beta^A\right)} \tag{121}$$

Note that $c_{Li^+}^{eq} = c_{Li^+} =$ concentration of Li$^+$ ion in the bulk electrolyte solution. The anode electrode reaction exchange current density, i_o^A, as shown by Eq. (121), is independent of the electric potential.

For the situation of the intercalated lithium diffusion in the cell cathode controlling the overall cell performance, it is likely, $c_{Li^+} = c_{Li^+}^{eq}$. Equation (116), then, reduces to

$$\left|i_s^A\right| = i_o^A \left[e^{\frac{(1-\beta^A)\eta_s^A F}{RT}} - e^{\frac{-\beta^A \eta_s^A F}{RT}} \right] \tag{122}$$

For low η_s^A values, i.e., for low $\left|i_s^A\right|$ values, Eq. (122) is reduced to

$$\left|i_s^A\right| = i_o^A \left(\frac{F}{RT}\right) \eta_s^A \tag{123}$$

This equation suggests that the experimental data on $\left|i_s^A\right|$ as a function of η_s^A can be employed to experimentally determine the anode electrode exchange current density, i_o^A; for its application in Eq. (122). Equation (122) can also be expressed as

$$\left|i_s^A\right| = i_o^A \left[e^{\frac{\alpha_a^A \eta_s^A F}{RT}} - e^{\frac{-\alpha_c^A \eta_s^A F}{RT}} \right] \tag{124}$$

where $\alpha_a^A = (1-\beta^A)n = (1-\beta^A) =$ anodic direction charge transfer coefficient across the cell anode-electrolyte interface, $\alpha_c^A = \beta^A n = \beta^A =$ cathodic direction charge transfer coefficient, (here, n=1).

For large current density, $\left|i_s^A\right|$, values, i.e., for $(\alpha_a^A \eta_s^A F) >> (RT)$; Eq. (124) reduces to

$$\left(\frac{\left|i^A\right|}{i_o^A}\right) = e^{\frac{\alpha_a^A \eta_s^A F}{RT}} \tag{125}$$

Take $\log_e$ of both sides of Eq. (125) to obtain

$$\ln\left(\frac{\left|i_s^A\right|}{i_o^A}\right) = \left(\frac{\alpha_a^A F}{RT}\right) \eta_s^A \tag{126}$$

This equation tells us that a plot of experimental data on $\ln\left(\dfrac{\left|i_s^A\right|}{i_o^A}\right)$ versus η_s^A should be a

straight line with its slope $= \dfrac{\alpha_a^A F}{RT}$. This could help one to determine α_a^A experimentally.

Because, here, for one electron reaction, $\left(\alpha_a^A + \alpha_c^A\right) = n = 1$; once α_a^A is known, one can

determine α_c^A. These experimentally determined charge transfer coefficients α_a^A and α_c^A can

then be used to compute the anode electrode charge transfer current density, or, the anode

electrode polarization voltage, η_s^A, for a current density, $\left|i_s^A\right|$ from Eq. (124).

For the intercalated lithium diffusion in the cathode active material controlling the cell overall behavior during the cell discharge period, the anode interfacial charge transfer current density, $\left|i_s^A\right|$, should be computed from

$$\left|i_s^A\right| = \frac{\left|I^{t,C}\right|}{A_g^A} \tag{127}$$

where A_g^A = geometric area of the cell anode electrode sheet in contact with the polymer electrolyte and $\left|I^{t,C}\right|$ = total cathode current as predicted by Eq. (39) or (41).

4.1.3.2 Reversible or Open-Circuit Potential of the Electrochemical Reaction at the Cell Anode

The electrochemical reaction occurring at the lithium anode-electrolyte is

$$\text{Li}(s) \;\square\; \text{Li}^+_{\text{(in electrolyte)}} + e^-_{\text{(in lithium metal)}} \tag{128}$$
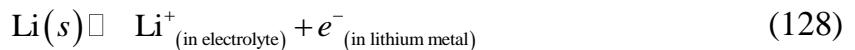
The thermodynamic equilibrium condition for the electrochemical reaction, Eq. (128), dictates that

$$\mu^{chem}_{\text{Li}(s)} = \mu^{echem}_{\text{Li}^+} + \mu^{echem}_{e^-} \tag{129}$$

$$\mu^{chem}_{\text{Li}(s)} = \left(\mu^{chem}_{\text{Li}^+\text{(in electrolyte)}} + z_{\text{Li}^+} F\Phi_{\text{electrolyte}}\right) + \left(\mu^{chem}_{e^-\text{(in Li metal)}} + z_{e^-} F\Phi^A_{\text{Li}(s)}\right) \tag{130}$$

This equation leads to

$$E^A_{rev} = \left(\Phi^A_{\text{Li}(s)} - \Phi_{\text{electrolyte}}\right) = \left(\frac{\mu^{chem}_{\text{Li}^+\text{(in electrolyte)}} + \mu^{chem}_{e^-\text{(in Li)}} - \mu^{chem}_{\text{Li}(s)}}{F}\right) \tag{131}$$

where E_{rev}^A = reversible electric potential of the electrochemical reaction, Eq. (128), occurring at the anode electrode; $\Phi_{Li(s)}^A$ = electrostatic potential in the lithium metal electrode, $\Phi_{electrolyte}$ = electrostatic potential in the electrolyte adjacent to the anode electrode just outside the double charge layer; $\mu_{Li^+(\text{in electrolyte})}^{chem}$, $\mu_{e^-(\text{in Li})}^{chem}$, and $\mu_{Li(s)}^{chem}$ are the chemical potentials of Li^+ ion in the electrolyte, electron in lithium metal, and of lithium metal of the cell anode electrode, respectively. The species chemical potentials are now expressed as

$$\mu_{Li^+(\text{in electrolyte})}^{chem} = \mu_{Li^+}^o + RT \ln a_{Li^+(\text{in electrolyte})} \tag{132}$$

$$\mu_{e^-(\text{in Li})}^{chem} = \mu_{e^-(\text{in Li})}^o + RT \ln a_{e^-(\text{in Li})} \tag{133}$$

$$\mu_{Li(s)}^{chem} = \mu_{Li(s)}^o + RT \ln a_{Li(s)} \tag{134}$$

where $\mu_{Li^+}^o$ = standard-state chemical potential of Li^+; the standard-state of Li^+ ion is here taken to be its state when present in 'the polymer solvent' in an infinitely small amount, e.g., $c_{Li^+}^o = 10^{-4} M$ concentration of Li^+ (or of $LiBF_4$ in the polymer electrolyte);

$a_{Li^+(\text{in electrolyte})} = \left(\gamma_{Li^+} \dfrac{c_{Li^+}}{c_{Li^+}^o} \right)$, $a_{e^-(\text{in Li})}$ = electron activity in lithium metal = 1 and $a_{Li(s)} = 1$ for pure lithium in the solid state at the electrode temperature; and $\mu_{Li^+}^o$, $\mu_{e^-(\text{in Li}(s))}^o$ and $\mu_{Li(s)}^o$ are the standard-state chemical potentials of Li^+ ion, electron, and lithium. The chemical potentials of these species are now expressed as

$$\mu_{Li^+(\text{in electrolyte})}^{chem} = \mu_{Li^+}^o + RT \ln \left(\gamma_{Li^+} \frac{c_{Li^+}}{c_{Li^+}^o} \right) \tag{135}$$

$$\mu_{e^-}^{chem} = \mu_{e^-(\text{in Li})}^o \tag{136}$$

$$\mu_{Li(s)}^{chem} = \mu_{Li(s)}^o \tag{137}$$

Inserting the above information for $\mu_{Li^+(\text{in electrolyte})}^{chem}$, $\mu_{e^-}^{chem}$, and $\mu_{Li(s)}^{chem}$ into Eq. (131) leads to

$$E_{rev}^A = E^{A,o} + \left(\frac{RT}{F} \right) \ln \left(\frac{\gamma_{Li^+} c_{Li^+}}{c_{Li^+}^o} \right) = E^{A,o} + \left(\frac{RT}{F} \right) \ln a_{Li^+} \tag{138}$$

$E^{A,o}$ = standard-state electric potential of the cell anode reaction, Eq. (128), at the anode temperature, and is given by

$$E^{A,o} = \left[\frac{\left(\mu^o_{\text{Li}^+} + \mu^o_{e^-} \right) - \mu^o_{\text{Li}(s)}}{F} \right] \qquad (139)$$

Equation (138) predicts that E^A_{rev} would increase as c_{Li^+} is increased. Note that the mathematical expression for E^A_{rev}, Eq. (138), derived using the basic thermodynamic principle for the cell anode reaction, Eq. (128), is similar to the electrokinetics based expression for E^A_{rev}, Eq. (120), with $c^{eq}_{\text{Li}^+} = c_{\text{Li}^+}$. In fact, comparison of Eqs. (138) and (120) leads to

$$\left(\frac{k^{A,1}_b}{k^A_{ff}} \right) = \exp \left[\frac{\left(\mu^o_{\text{Li}^+} + \mu^o_{e^-} \right) - \mu^o_{\text{Li}(s)}}{RT} \right] \qquad (140)$$

Equation (140) relates the cell anode reaction rate coefficients at a temperature and the standard-state chemical potentials of the species involved in the anode reaction, μ^o_i. The reciprocal of Eq. (140) leads to

$$\left(\frac{k^A_{ff}}{k^{A,1}_b} \right) = K^A = e^{-\frac{\left\{ \left(\mu^o_{\text{Li}^+} + \mu^o_{e^-} \right) - \mu^o_{\text{Li}(s)} \right\}}{RT}} = e^{-\frac{\Delta G^o}{RT}} \qquad (141)$$

Notice that Eq. (141) is the mathematical expression for the thermodynamic equilibrium constant at a temperature, $T[K]$, where one needs to know the standard-state Gibbs free energy of the reaction, Eq. (128).

4.1.4 Reversible or Open-Circuit Potential of the Lithium-Based Cell

The cell reversible potential at a temperature is given by

$$E^{cell}_{rev} = E^C_{rev} - E^A_{rev} \qquad (142)$$

Inserting the expressions for E^C_{rev} and E^A_{rev} from Eqs. (62) and (138), respectively, into Eq. (142), leads; for the cell overall reaction, $\text{Li}(s) \square$ Li-in 'the solid state solvent $M_y Pc'$, to

$$E^{cell}_{rev} = \left(\frac{\mu^o_{\text{Li}(s)} - \mu^o_{\text{Li-in } M_y Pc}}{F} \right) - \left(\frac{RT}{F} \right) \ln \left(\frac{x}{x^o} \gamma_{\text{Li-in } M_y Pc} \right) \qquad (143)$$

On rewriting Eq. (143),

$$E_{rev}^{cell} = E^{cell,o} - \left(\frac{RT}{F}\right)\ln\left(\gamma_{\text{Li-in M}_y\text{Pc}}\frac{x}{x^o}\right) \tag{144}$$

$$E_{rev}^{cell} = E^{cell,o} - \left(\frac{RT}{F}\right)\ln a_{\text{Li-in M}_y\text{Pc}} \tag{145}$$

where

$$E^{cell,o} = \frac{\mu_{\text{Li}(s)}^o - \mu_{\text{Li-in M}_y\text{Pc}}^o}{F} \tag{146}$$

$$E^{cell,o} = -\frac{\Delta G^o}{F} \tag{147}$$

where $\Delta G^o = \mu_{\text{Li-in M}_y\text{Pc}}^o - \mu_{\text{Li}(s)}^o =$ standard-state Gibbs free energy change for the overall cell reaction: $\text{Li}(s) \,\square\, \left(\text{Li-intercalated in the solid-state solvent M}_y\text{Pc of the cell cathode}\right)$. Note that as $x \to x^o$, $\gamma_{\text{Li-in M}_y\text{Pc}} \to 1.0$; then, Eq. (144) leads to:

$$\lim_{x \to x^o}\left[E_{rev}^{cell}\right] = E^{cell,o} \tag{148}$$

This equation tells us that with a selected standard-state of lithium in M_yPc, i.e., with a selected or defined value of x^o, e.g., $x^o = 10^{-9}$ $g\text{-}mole$ of the intercalated lithium per $g\text{-}mole$ of initial M_yPc, one can experimentally determine $E^{cell,o}$ at a given cell temperature, $T[K]$, simply by the measurement of voltage difference between the cell anode and cathode electrodes at the cathode composition state of x^o. Then, one should experimentally measure E_{rev}^{cell} as a function of the intercalated lithium, x, in M_yPc at the same temperature for which $E^{cell,o}$ has been experimentally determined. Using Eq. (144) one can compute $\gamma_{\text{Li-in M}_y\text{Pc}}$ as a function of $\left(\dfrac{x}{x_o}\right)$.

One should, then, develop an empirical correlation for $\gamma_{\text{Li-in M}_y\text{Pc}}$ or $a_{\text{Li-in M}_y\text{Pc}}$ in terms of $\left(\dfrac{x}{x_o}\right)$ at one cell temperature. This procedure should be used for at least three temperatures. The empirically developed such correlations at different temperatures can then be used to predict the reversible cell voltage at any x value during the cell discharge period. One should be aware of that the cell reversible voltage is needed to predict the cell performance, i.e., actual power provided by the cell during its discharge.

4.1.5   Cell Performance during the Period of its Discharge

If the overall performance behavior of the lithium-ion cell shown in the sketch, Fig. 1, is controlled by the lithium diffusion in the cathode, M_yPc, material; then, the concentration polarization or voltage loss in the electrolyte can be assumed to be negligible due to negligible ion or electrolyte concentration gradient. At any time, total cell current can be predicted using Eq. (39) or (41) and total charge transferred from the cell anode to cathode using Eq. (40) or (42). The lithium content in cathode initial material, M_yPc, during the cell discharge period at any time can be computed from the following result obtained using Eq. (40) or (42)

$$x = x^{ini} + \left(x_o - x^{ini}\right)\left[\sum_{i=1}^{i=N_p} w_{pi,o}\left\{1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{\exp\left(-n^2\pi^2\overline{\tau}_{pi,o}\right)}{n^2}\right\}\right] \tag{149}$$

(for the cathode active material particle size distribution)

Or,

$$x = x^{ini} + \left(x_o - x^{ini}\right)\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{\exp\left(-n^2\pi^2\overline{\tau}_{p,o}\right)}{n^2}\right] \tag{150}$$

(for the cathode active material particles of uniform or same size)

In Eq. (149) or (150), $x_o = g$-*moles* of the intercalated lithium per *g-mole* of initial M_yPc in the cathode active material M_yPc at the electrolyte-active material particle interface; $x^{ini} =$ initial *g-moles* of the intercalated lithium per *g-mole* of initial M_yPc in an active material particle; and $N_p =$ total number of active material particle size ranges. One should compute the cell reversible or open-circuit electric potential from Eq. (144). The ohmic voltage losses in the cathode electrolyte and the cathode carbon electronic conductor should be computed from Eqs. (46) and (48), respectively. The ohmic voltage loss in the electrolyte separator is to be computed from Eq. (100). The cathode activation and anode activation polarizations or voltage losses should be computed at any time from Eq. (91), (92), or (93) for the cathode activation polarization, $\left(-\eta_s^C\right)$, and from Eq. (124) for the anode activation polarization, η_s^A. The cell voltage at any time during the cell discharge period should then be computed from the following equation

$$V^{cell} = E_{rev}^{cell} - \left[\left|\Delta\Phi_{electrolyte}^S\right|_\Omega + \left|\Delta\Phi_{electrolyte}^C\right|_\Omega + \left|\Delta\Phi_{electron}^{C-carbon}\right|_\Omega + \left|\left(-\eta_s^C\right)\right| + \left|\eta_s^A\right|\right] \tag{151}$$

where $E_{rev}^{cell} =$ cell reversible voltage; $V^{cell} =$ actual voltage difference between the cell anode and cathode electrodes; $\left|\Delta\Phi_{electrolyte}^S\right|_\Omega$, $\left|\Delta\Phi_{electrolyte}^C\right|_\Omega$, and $\left|\Delta\Phi_{electron}^{C-carbon}\right|_\Omega$ are the ohmic voltage losses in the cell electrolyte separator, cathode electrode electrolyte, and cathode carbon

electronic conductor, respectively; and $\left|\left(-\eta_s^C\right)\right|$ and $\left|\eta_s^A\right|$ are the cathode and anode electrode activation polarization voltage losses, respectively. The actual electric power delivered by the cell during the cell discharge period at any time is given by

$$\dot{P} = I^t V^{cell} = I^{t,C} V^{cell} \tag{152}$$

for the cell current $I^t = I^{t,C}$ (current limited by the lithium diffusion in the cathode active material particles). The thermodynamic efficiency at any time may be defined as

$$\eta_{\text{thermody}} = \frac{I^{t,C} V^{cell}}{I^{t,C} E_{rev}^{cell}} = \frac{V^{cell}}{E_{rev}^{cell}} \tag{153}$$

4.1.6 Cathode Active Material Spherical Particle Utilization to Store Lithium (i.e. Coulomb Efficiency of a Cathode Active Material Particle) during the Cell Discharge Period

The formulation to predict the transient lithium concentration profiles in a spherical particle of a cathode active material as a function of the dimensionless radial distance is provided for a constant lithium ion flux or a constant electrolyte-cathode active material particle interfacial current density. This formulation is then employed to develop the mathematical expression to predict the coulomb efficiency of the cell cathode consisted of uniform-sized active material spherical particles under the condition of lithium diffusion in the particles controlling the overall cell discharge process.

The partial differential equation (PDE) describing lithium diffusion in a spherical particle of the cathode active material is

$$\frac{\partial c}{\partial t} = \frac{\bar{D}}{r^2} \frac{\partial}{\partial r}\left(r \frac{\partial c}{\partial r}\right) \tag{154}$$

The initial and boundary conditions are:

$$t \le 0, c = c_{ini} \tag{155}$$

$$t > 0, r = 0, c = finite \tag{156}$$

or, the boundary condition represented by Eq. (156) can also be given by

$$t > 0, \left(\frac{\partial c}{\partial r}\bigg|_{r=0}\right) = 0 \tag{157}$$

(symmetry of the intercalated lithium concentration with respect to the radial distance at the spherical particle center)

The second boundary condition, at $r = a$ (particle surface), is given by

$$t > 0, r = a, \bar{D}\left(\frac{\partial c}{\partial r}\bigg|_{r=a}\right) = J_s = \frac{|i_s^C|}{F} \tag{158}$$

where $\bar{D}$ = lithium mass diffusivity averaged over lithium concentration in the cathode active material particle, J_s = lithium ion molar flux at the particle surface; assumed here to be constant, $|i_s^C|$ = magnitude of the electrolyte-active material particle interfacial current density; assumed to be constant, F = Faraday's constant = 96487 coulomb per g-mole of Li^+ (or per g-equivalent).

The solution to the PDE, Eq. (154), for the initial and boundary conditions, Eqs. (155) through (158) is adopted from [3] and is given below.

$$\left[\frac{\bar{D}(c - c_{ini})}{J_s a}\right] = \frac{\bar{D}(x - x_{ini})\rho_{cathode}}{(J_s a)M_{cathode}}$$

$$= \left[3\tau + \frac{\xi^2}{2} - 0.3 - 2\sum_{n=1}^{n=\infty} \frac{\sin\{(a\alpha_n)\xi\}}{\xi(a\alpha_n)^2 \sin(a\alpha_n)} \cdot \exp\left(-\tau(a\alpha_n)^2\right)\right] \tag{159}$$

where $\tau = \dfrac{\bar{D}t}{a^2}$, $\xi = \dfrac{r}{a}$, x = moles of the intercalated lithium per mole of the cathode active material at any location ξ in the active material particle, x_{ini} = initial moles of lithium per mole of the cathode active material, $\rho_{cathode}$ = cathode active material particle density, and $M_{cathode}$ = mol. wt. of the cathode active material. The $(a\alpha_n)$s are the roots of the following mathematical expression:

$$(a\alpha_n)\cot(a\alpha_n) = 1 \tag{160}$$

Positive roots of Eq. (160) are

$$\left[\begin{array}{l}(a\alpha_1) = 4.4934, (a\alpha_2) = 7.7253, (a\alpha_3) = 10.9041, \\ (a\alpha_4) = 14.0662, (a\alpha_5) = 17.2208, \text{ etc.}\end{array}\right] \tag{161}$$

At the particle center, i.e., at $\xi = 0$, Eq. (159) reduces to:

$$\left[\frac{\bar{D}(c_{center} - c_{ini})}{J_s a}\right] = \frac{\bar{D}(x_{center} - x_{ini})\rho_{cathode}}{(J_s a)M_{cathode}} = \left[3\tau - 0.3 - 2\sum_{n=1}^{n=\infty} \frac{\exp\left(-\tau(a\alpha_n)^2\right)}{(a\alpha_n)\sin(a\alpha_n)}\right] \tag{162}$$

Equation (162) predicts the lithium concentration at the spherical particle center as a function

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of $\tau = \dfrac{\bar{D}t}{a^2}$.

At the particle surface, i.e., at $\xi = 1$, Eq. (159) leads to:

$$\left[\frac{\bar{D}(c_s - c_{ini})}{J_s a}\right] = \frac{\bar{D}(x_s - x_{ini})\rho_{cathode}}{(J_s a)M_{cathode}} = \left[3\tau + 0.2 - 2\sum_{n=1}^{n=\infty}\frac{\exp\left(-\tau(a\alpha_n)^2\right)}{(a\alpha_n)^2}\right] \qquad (163)$$

Equation (163) predicts the lithium concentration at the spherical particle surface as a function of the dimensionless time, $\tau\left(= \dfrac{\bar{D}t}{a^2}\right)$.

If the time for lithium concentration at the cathode active material particle surface to reach $c_s^{sat'd}$ is $t_s^{sat'd}$, then the amount of lithium that would have accumulated in the particle by this time is given by

$$N_{\text{Li-surface sat'd}}^{t\text{-actual}} = 4\pi a^2 J_s t_s^{sat'd} \qquad (164)$$

It should be noted that when c_s becomes equal to $c_s^{sat'd}$ during the cell discharge, cell voltage would drop steeply and the cell then must be declared discharged. The amount of lithium required to be transferred or intercalated to uniformly saturate the spherical particle is given by

$$N_{\text{Li}}^{t\text{-sat'd}} = \left(\frac{4}{3}\pi a^3\right)\left[\left(x^{sat'd} - x_{ini}\right)\frac{\rho_{\text{cathode-active material}}}{M_{\text{cathode-active material}}}\right] \qquad (165)$$

The cathode active material utilization or its coulomb efficiency to store lithium during the cell discharge period is defined as

$$U = \left[\frac{N_{\text{Li-surface sat'd}}^{t\text{-actual}}}{N_{\text{Li}}^{t\text{-sat'd}}}\right] \qquad (166)$$

Using the information from Eqs. (164) and (165) in Eq. (166) leads to:

$$U = 3\left[\frac{J_s\left(\dfrac{t_s^{sat'd}}{a}\right)}{\left(\dfrac{\left(x^{sat'd} - x_{ini}\right)\rho_{\text{cathode-active material}}}{M_{\text{cathode-active material}}}\right)}\right] \qquad (167)$$

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Equation (167) is now expressed as

$$U = \left[\frac{3\tau_s^{sat'd}}{\left[\left(\dfrac{\bar{D}\left(x_s^{sat'd} - x_{ini}\right)\rho_{cathode}}{\left(J_s a\right)M_{cathode}} \right) \right]} \right] \tag{168}$$

From Eq. (163),

$$\left(\frac{\bar{D}\left(x_s^{sat'd} - x_{ini}\right)\rho_{cathode}}{\left(J_s a\right)M_{cathode}} \right) = \left[3\tau_s^{sat'd} + 0.2 - 2\sum_{n=1}^{n=\infty} \frac{\exp\left(-\tau_s^{sat'd}\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2} \right] \tag{169}$$

Inserting the information from Eq. (169) into Eq. (168) leads to

$$U = \left[\frac{3\tau_s^{sat'd}}{\left\{ 3\tau_s^{sat'd} + 0.2 - 2\sum_{n=1}^{n=\infty} \frac{\exp\left(-\tau_s^{sat'd}\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2} \right\}} \right] \tag{170}$$

where. $\tau_s^{sat'd} = \dfrac{\bar{D}t_s^{sat'd}}{a^2}$.

Numerical assessment of $\displaystyle\sum_{n=1}^{n=\infty}\exp\left(\frac{-\tau_s^{sat'd}\left(a\alpha_n\right)^2}{\left(a\alpha_n\right)^2}\right)$ indicates that this sum makes negligible

contribution to the function shown in the denominator of the right-hand side of Eq. (170) for $\tau_s^{sat'd} \geq 1$. So, Eq. (170) is written as

$$U = \frac{3\tau_s^{sat'd}}{3\tau_s^{sat'd} + 0.2} \tag{171}$$

valid for. $\tau_s^{sat'd} \geq 1$.

One should use Eq. (170) to compute U for $\tau_s^{sat'd} < 1$ and Eq. (171) for $\tau_s^{sat'd} \geq 1$.

Once U, the cathode active material particle collection efficiency, has been determined using Eq. (170) or (171) for a fixed $t_s^{sat'd}$ and a particle radius; then one should compute the lithium ion flux at the electrolyte-active material interface, J_s, from Eq. (168). Then, corresponding to the

computed J_s value, one should determine the electrolyte-cathode active material particle interfacial current density, i_s^C.

$$i_s^C = J_s F \tag{172}$$

To show the effect of the cathode active material particle radius on U, J_s, and i_s^C, one should compute them for a selected $t_s^{sat'd}$ value (e.g. $t_s^{sat'd} = 3600$ seconds) for a given cathode material as a function of particle radius, a or $\tau_s^{sat'd}$ (dimensionless time for the particle surface saturation). For the practical application of such computed data in the design and performance analysis of a cathode of a given material, one should develop plots of U, J_s, and i_s^C as a function of $\tau_s^{sat'd}$ and the active material particle diameter, $2a$, for $t_s^{sat'd} = 3600$ secs.

In what follows the development of the formulation to compute the transient lithium concentration profiles in a cathode active material, spherical particle for the short time condition is briefly presented. This formulation should only be used when the cell discharge period is so short that the intercalated lithium concentration at the particle surface would have reached the saturation level while the lithium penetration toward the particle center, via the molecular diffusion process, is still in the spatial region very near the particle surface.

The flux distribution of the intercalated lithium inside the cathode active material particle is given by the following partial differential equation (PDE) [8].

$$\frac{\partial c}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 J_r\right) \tag{173}$$

where c = molar concentration of the intercalated lithium at any radial position, r, at any time, t, inside the cathode spherical particle and J_r = lithium diffusion flux along the radial position; it is positive if lithium diffuses away from the particle center and negative if its diffusion is toward the particle center. The radial diffusion flux J_r is expressed as

$$J_r = \bar{D}\left(-\frac{\partial c}{\partial r}\right) \tag{174}$$

Differentiating the PDE, Eq. (173), with respect to r and using the expression for J_r in Eq. (174) with constant $\bar{D}$ leads to

$$\frac{\partial J_r}{\partial t} = \bar{D}\frac{\partial}{\partial r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 J_r\right)\right] \tag{175}$$

For the situation of short times, lithium ions after reduction and entering the active material particle diffuse (as $Li^+ + e^-$) toward the particle center. It is, however, assumed that they stay

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near the particle surface until the lithium concentration at the particle surface located at $r = a$ reaches the saturation level of $c_s^{sat'd}$ or $x_s^{sat'd}$; where $c_s^{sat'd} =$ saturated molar concentration and $x_s^{sat'd} = g\text{-}moles$ of lithium per $g\text{-}mole$ of the cathode active material at the saturation level. The intercalated lithium $\left(\left(Li^+ + e^-\right) = Li\right)$ atoms 'see' the particle spatial region away from "a very thin spatial region near the particle surface" as if it is not approachable during the cell discharge period until the lithium concentration at the particle periphery reaches the saturation level. For this situation, the lithium diffusion inside the cathode active material particle is very near the particle surface. Therefore, the PDE, Eq. (175) is rewritten, with the assumption of $r \to a$, as follows.

$$\frac{\partial J_r}{\partial t} \cong \bar{D}\frac{\partial}{\partial r}\left[\frac{1}{a^2}\frac{\partial}{\partial r}\left(a^2 J_r\right)\right] \tag{176}$$

Equation (176) becomes

$$\frac{\partial J_r}{\partial t} = \bar{D}\frac{\partial}{\partial r}\left[\frac{\partial}{\partial r}J_r\right] \tag{177}$$

Position of a spatial point inside the cathode active material particle is expressed as

$$y = a - r \tag{178}$$

where $y =$ distance of the spatial point measured from the particle surface and $r =$ distance of the same spatial point measured from the particle center along a particle radius. Note that at $r = a$, $y = 0$ and at $r = 0$, $y = a$ and $\frac{dy}{dr} = -1$.

Now,

$$\frac{\partial J_r}{\partial r} = \left(\frac{\partial J_r}{\partial y}\cdot\frac{dy}{dr}\right) = -\frac{\partial J_r}{\partial y} \tag{179}$$

knowing, $\dfrac{\partial}{\partial r}\left[\dfrac{\partial J_r}{\partial r}\right] = \dfrac{\partial}{\partial r}\left[-\dfrac{\partial J_r}{\partial y}\right] = -\dfrac{\partial}{\partial r}\left[\dfrac{\partial J_r}{\partial y}\right] = -\left[\dfrac{\partial}{\partial y}\left(\dfrac{\partial J_r}{\partial y}\right)\dfrac{dy}{dr}\right]$

Hence,

$$\frac{\partial^2 J_r}{\partial r^2} = -\left[\frac{\partial}{\partial y}\left(\frac{\partial J_r}{\partial y}\right)(-1)\right] = \frac{\partial^2 J_r}{\partial y^2} \tag{180}$$

Inserting the information from Eq. (180) for $\dfrac{\partial^2 J_r}{\partial r^2}$ into Eq. (177) leads to

$$\frac{\partial J_r}{\partial t} = \bar{D}\frac{\partial^2 J_r}{\partial y^2} \tag{181}$$

Note that $J_r\left(=\left|J_r\right|\right)$ has a positive number value with respect to y.

Divide both sides of Eq. (181) by $J_s = \dfrac{\left|i_s^C\right|}{F}$, the lithium molar flux at the particle surface along the radial distance toward the particle center corresponding to a fixed electrolyte-active material particle interfacial current density $\left|i_s^C\right|$. The PDE, Eq. (181) becomes

$$\frac{\partial \Gamma}{\partial t} = \bar{D}\frac{\partial^2 \Gamma}{\partial y^2} \tag{182}$$

where

$$\Gamma = \left(\frac{J_r}{J_s}\right) \tag{183}$$

The initial and boundary conditions to solve the PDE, Eq. (182), are

I.C.: For $t \leq 0$,
$$\Gamma = 0, \text{ for, } 0 \leq y \leq a \tag{184}$$
B.C.1: For $t > 0$,
$$\Gamma = 1, \text{ at } y = 0 \text{ (at the particle surface)} \tag{185}$$
B.C.2: For $t > 0$,
$$\Gamma = 0, \text{ at } y \to \text{"}\infty\text{"} \tag{186}$$

Here the PDE, Eq. (182), is solved using the method of combination of independent variables. A dimensionless quantity, η, is defined as

$$\eta = \frac{y}{\sqrt{4\bar{D}t}} \tag{187}$$

Now the PDE, Eq. (182), and the initial and boundary conditions are transformed into the dimensionless form.

$$\frac{\partial \Gamma}{\partial t} = \frac{d\Gamma}{d\eta} \cdot \frac{\partial \eta}{\partial t} = \frac{d\Gamma}{d\eta} \cdot \frac{\partial}{\partial t}\left(\frac{y}{\sqrt{4\bar{D}t}}\right) = \frac{d\Gamma}{d\eta}\left(\frac{y}{\sqrt{4\bar{D}}}\right)\frac{d}{dt}\left(\frac{1}{\sqrt{t}}\right)$$

$$= \left(\frac{d\Gamma}{d\eta}\right)\left(\frac{y}{\sqrt{4\bar{D}t}}\right)\left(-\frac{1}{2t}\right) = \left(-\frac{\eta}{2t}\right)\frac{d\Gamma}{d\eta} \tag{188}$$

$$\frac{\partial \Gamma}{\partial y} = \frac{d\Gamma}{d\eta} \cdot \frac{\partial \eta}{\partial y} = \frac{d\Gamma}{d\eta} \cdot \frac{\partial}{\partial y}\left(\frac{y}{\sqrt{4\bar{D}t}}\right)$$

$$= \frac{d\Gamma}{d\eta}\left(\frac{1}{\sqrt{4\bar{D}t}}\right)\left(\frac{dy}{dy}\right) = \left(\frac{1}{\sqrt{4\bar{D}t}}\right)\frac{d\Gamma}{d\eta} \tag{189}$$

Differentiating both sides of Eq. (189) with respect to y,

$$\frac{\partial^2 \Gamma}{\partial y^2} = \frac{\partial}{\partial y}\left[\left(\frac{1}{\sqrt{4\bar{D}t}}\right)\frac{d\Gamma}{d\eta}\right] = \left(\frac{1}{\sqrt{4\bar{D}t}}\right)\frac{\partial}{\partial y}\left(\frac{d\Gamma}{d\eta}\right)$$

$$= \frac{1}{\sqrt{4\bar{D}t}}\left[\frac{d}{d\eta}\left(\frac{d\Gamma}{d\eta}\right)\frac{\partial \eta}{\partial y}\right] \tag{190}$$

thus,

$$\frac{\partial^2 \Gamma}{\partial y^2} = \frac{1}{\sqrt{4\bar{D}t}} \cdot \frac{d^2\Gamma}{d\eta^2} \cdot \frac{1}{\sqrt{4\bar{D}t}} = \left(\frac{1}{4\bar{D}t}\right)\frac{d^2\Gamma}{d\eta^2} \tag{191}$$

Inserting the mathematical expressions for $\dfrac{\partial \Gamma}{\partial t}$ and $\dfrac{\partial^2 \Gamma}{\partial y^2}$ from Eqs. (189) and (190), respectively, into Eq. (182) and simplifying leads to

$$\frac{d^2\Gamma}{d\eta^2} + 2\eta\frac{d\Gamma}{d\eta} = 0 \tag{192}$$

The initial and boundary conditions in the transformed form are

I.C.:
$$\text{at } \eta = \infty, \Gamma = 0 \tag{193}$$
B.C.1:
$$\text{at } \eta = 0, \Gamma = 1 \tag{194}$$
B.C.2:
$$\text{at } \eta = \infty, \Gamma = 0 \tag{195}$$

Noting that the initial and B.C.2 conditions are identical, the above conditions are now rewritten as

B.C.1:

$$\text{at } \eta = 0, \Gamma = 1 \tag{196}$$

B.C.2:

$$\text{at } \eta = \infty, \Gamma = 0 \tag{197}$$

Now, the differential Eq. (192) is solved using the boundary conditions, Eqs. (196) and (197).

Let,

$$\frac{d\Gamma}{d\eta} = \psi \tag{198}$$

Therefore,

$$\frac{d^2\Gamma}{d\eta^2} = \frac{d\psi}{d\eta} \tag{199}$$

Inserting the information from Eqs. (198) and (199) for $\dfrac{d\Gamma}{d\eta}$ and $\dfrac{d^2\Gamma}{d\eta^2}$, respectively, into Eq. (192) leads to

$$\frac{d\psi}{d\eta} + 2\eta\psi = 0 \tag{200}$$

Separating the variables,

$$\frac{d\psi}{\psi} = -2\eta d\eta \tag{201}$$

Integration of both sides of Eq. (201) leads to

$$\log_e \psi = -\eta^2 + A_1 \tag{202}$$

Simplification of Eq. (202) leads to

$$\psi = e^{-\eta^2 + A_1} = \left(e^{A_1}\right)e^{-\eta^2} = Ae^{-\eta^2} \tag{203}$$

Inserting the expression for ψ from Eq. (203) into Eq. (198) leads to

$$\frac{d\Gamma}{d\eta} = Ae^{-\eta^2} \tag{204}$$

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$$dΓ = Ae^{-η^2} dη \tag{205}$$

Integrating both sides of Eq. (205),

$$Γ = A\int_0^η e^{-η^2} dη + B \tag{206}$$

Rewriting Eq. (206),

$$Γ = A\int_{u=0}^{u=η} e^{-u^2} du + B \tag{207}$$

where u = 'dummy variable' for $η$, and B = second constant of integration. Now, the integration constants A and B are evaluated using the boundary conditions, Eqs. (196) and (197).

$$\left(Γ\big|_{\text{at } u=η=0}\right) = A\left[\int_{u=0}^{u=η} e^{-u^2} du\right]\Bigg|_{u=η=0} + B \tag{208}$$

$$\left(Γ\big|_{\text{at } u=η=∞}\right) = A\left[\int_{u=0}^{u=η} e^{-u^2} du\right]\Bigg|_{u=η=∞} + B \tag{209}$$

The expressions in Eqs. (208) and (209) lead to

$$1 = A\left(\int_{u=0}^{u=0} e^{-u^2} du\right) + B \tag{210}$$

$$0 = A\left(\int_{u=0}^{u=∞} e^{-u^2} du\right) + B \tag{211}$$

The solution to Eqs. (210) and (211) for A and B leads to

$$B = 1 \tag{212}$$

and

$$A = -\frac{1}{\int_0^∞ e^{-u^2} du} \tag{213}$$

Substituting for *B* and *A* from Eqs. (212, 213) into Eq. (207) leads to

$$\Gamma = 1 - \frac{\int\limits_0^\eta e^{-u^2} du}{\int\limits_0^\infty e^{-u^2} du} \tag{214}$$

$$= 1 - \frac{\dfrac{2}{\sqrt{\pi}} \int\limits_0^\eta e^{-u^2} du}{\left(\dfrac{2}{\sqrt{\pi}} \int\limits_0^\infty e^{-u^2} du \right)} \tag{215}$$

$$\Gamma = 1 - \left(\frac{2}{\sqrt{\pi}} \right) \frac{\int\limits_0^\eta e^{-u^2} du}{erf(\infty)} = 1 - \frac{2}{\sqrt{\pi}} \int\limits_0^\eta e^{-u^2} du \tag{216}$$

because $erf(\infty) = 1$.

Rewriting Eq. (216),

$$\Gamma = \frac{J_r}{J_s} = 1 - erf(\eta) = erfc(\eta) \tag{217}$$

where the error function of η, $erf(\eta) = \dfrac{2}{\sqrt{\pi}} \int\limits_0^\eta e^{-u^2} du$ and the complementary error function of

η,

$erfc(\eta) = \dfrac{2}{\sqrt{\pi}} \int\limits_{u=\eta}^{u=\infty} e^{-u^2} du = 1 - erf(\eta)$ and

$$\eta = \frac{y}{\sqrt{4\bar{D}t}} = \frac{(y/a)}{\left(\dfrac{1}{a}\right)\sqrt{4\bar{D}t}} = \frac{(y/a)}{\sqrt{4}\sqrt{\dfrac{\bar{D}t}{a^2}}} = \frac{Y}{2\sqrt{\tau}} \tag{218}$$

where the dimensionless distance $Y = \dfrac{y}{a}$ and $\tau = \left(\dfrac{\bar{D}t}{a^2} \right)$, dimensionless time.

One can predict $\Gamma\left(=\dfrac{J_r}{J_s}\right)$ as a function of η or Y at each $\tau=\left(\dfrac{\bar{D}t}{a^2}\right)$ or t value using Eq. (217).

At $\eta=2$, $erfc(\eta)\cong 0.01$. Therefore, a mass transfer boundary-layer thickness, δ_m, is defined corresponding to:

$$\eta=\frac{Y}{2\sqrt{\tau}}=\frac{y}{2a\sqrt{\tau}}=\frac{\delta_m}{2a\sqrt{\tau}}=2 \tag{219}$$

The mass-transfer boundary-layer thickness, δ_m, is then given by

$$\delta_m=4a\sqrt{\tau}=4\sqrt{\bar{D}t} \tag{220}$$

The mass-transfer boundary-layer thickness, δ_m, is a natural length scale for the lithium ion mass flux in a cathode active material, spherical particle. The distance, δ_m, is a measure of the extent to which lithium ions have penetrated into a particle of the cell cathode active material in the elapsed time, t. It is proportional to $\sqrt{t}$.

To obtain the lithium concentration, c, distribution in a spherical particle of the cathode active material, the lithium ion flux inside the particle toward the particle center is expressed by

$$J_r=-\bar{D}\frac{\partial c}{\partial r} \tag{221}$$

Because, $r=a-y$; therefore,

$$dr=-dy \tag{222}$$

From Eq. (221),

$$J_r=-\bar{D}\frac{\partial c}{\left(-\partial y\right)}=\bar{D}\frac{\partial c}{\partial y} \tag{223}$$

Rearranging Eq. (223) and integrating the resulting expression leads to

$$\int_c^{c_{ini}}dc=\int_y^\infty\left(\frac{J_r}{\bar{D}}\right)dy \tag{224}$$

$$\left(c_{ini}-c\right)=\int_y^\infty\left(\frac{J_r}{\bar{D}}\right)dy \tag{225}$$

Or,

$$(c - c_{ini}) = \int_y^\infty \frac{(-J_r)}{\bar{D}} dy = \int_y^\infty \left[\frac{J_s\left(\dfrac{-J_r}{J_s}\right)}{\bar{D}} \right] dy \tag{226}$$

$$= \int_y^\infty \frac{J_s\Gamma}{\bar{D}} dy \tag{227}$$

where $\Gamma = \left(\dfrac{-J_r}{J_s}\right) = \dfrac{|J_r|}{J_s}$ or simply;

$$\Gamma = \frac{J_r}{J_s} \tag{228}$$

With the assumption of constant $\bar{D}$, Eq. (227) leads to

$$(c - c_{ini}) = \left(\frac{J_s}{\bar{D}}\right) \int_y^\infty \Gamma dy \tag{229}$$

Because $\eta = \dfrac{y}{\sqrt{4\bar{D}t}}$; therefore, $\dfrac{\partial \eta}{\partial y} = \dfrac{1}{\sqrt{4\bar{D}t}}$. This result leads to:

$$dy = \sqrt{4\bar{D}t}\, d\eta \tag{230}$$

Substitution for dy from Eq. (230) into Eq. (229) and simplification leads to

$$(c - c_{ini}) = J_s\left(\sqrt{\frac{4t}{\bar{D}}}\right) \int_\eta^\infty \Gamma d\eta \tag{231}$$

Substitution for Γ from Eq. (217) into Eq. (231) leads to

$$(c - c_{ini}) = J_s\left(\sqrt{\frac{4t}{\bar{D}}}\right) \int_\eta^\infty \left[erfc(\eta) \right] d\eta \tag{232}$$

$$= J_s\left(\sqrt{\frac{4t}{\bar{D}}}\right) \int_\eta^\infty \left[\frac{2}{\sqrt{\pi}} \int_{u=\eta}^{u=\infty} e^{-u^2} du \right] d\eta \tag{233}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \int\limits_{\eta}^{\infty} \left[\int\limits_{u=\eta}^{u=\infty} e^{-u^2} du \right] d\eta \tag{234}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{\zeta=\eta}^{\zeta=\infty} \left[\int\limits_{\eta}^{\infty} e^{-u^2} du \right] d\zeta \right] \tag{235}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{u=\eta}^{u=\infty} \left\{ \int\limits_{\zeta=\eta}^{\zeta=u} e^{-u^2} d\zeta \right\} du \right] \tag{236}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{u=\eta}^{u=\infty} \left\{ e^{-u^2} \left(\zeta \right)_{\zeta=\eta}^{\zeta=u} \right\} du \right] \tag{237}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{u=\eta}^{u=\infty} \left\{ e^{-u^2} \left(u - \eta \right) \right\} du \right] \tag{238}$$

$$= J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{u=\eta}^{u=\infty} \left\{ u e^{-u^2} - \eta e^{-u^2} \right\} du \right] \tag{239}$$

Therefore,

$$\left(c - c_{ini} \right) = J_s \left(\frac{16t}{\pi \bar{\bar{D}}} \right)^{\frac{1}{2}} \left[\int\limits_{\eta}^{\infty} u e^{-u^2} du - \eta \int\limits_{u=\eta}^{u=\infty} e^{-u^2} du \right] \tag{240}$$

with $u^2 = z, u\,du = \dfrac{dz}{2}$

$$\int\limits_{\eta}^{\infty} u e^{-u^2} du = \frac{1}{2} \int\limits_{z=\eta^2}^{z=\infty} e^{-z} dz = \left(-\frac{1}{2} \right) \left[e^{-z} \right]_{z=\eta^2}^{z=\infty} \tag{241}$$

$$\int\limits_{\eta}^{\infty} u e^{-u^2} du = \left(\frac{e^{-\eta^2}}{2} \right) \tag{242}$$

Substitution for $\left[\int\limits_{\eta}^{\infty} u e^{-u^2} du \right]$ from Eq. (242) into Eq. (240) leads to

$$(c - c_{ini}) = J_s \left(\frac{16t}{\pi \bar{D}} \right)^{\frac{1}{2}} \left[\frac{e^{-\eta^2}}{2} - \eta \int_{u=\eta}^{u=\infty} e^{-u^2} du \right] \qquad (243)$$

where $\eta = \dfrac{Y}{2\sqrt{\tau}}$, $\tau = \dfrac{\bar{D}t}{a^2}$ and $Y = \dfrac{y}{a}$.

Note: See Ref. [9] for direct use of the formula for $\displaystyle\int_{\eta}^{\infty} \left[erfc(\eta) \right] d\eta$.

Equation (243) is changed to the following form.

$$(c - c_{ini}) = \left(\frac{J_s a}{\bar{D}} \right) \cdot \sqrt{\tau} \cdot \sqrt{\frac{16}{\pi}} \left[\frac{1}{2e^{\eta^2}} - \eta \int_{u=\eta}^{u=\infty} e^{-u^2} du \right] \qquad (244)$$

$$(c - c_{ini}) = \left(\frac{J_s a}{\bar{D}} \right) \left(\sqrt{\frac{4}{\pi}} \right) (2\sqrt{\tau}) \left[\frac{1}{2e^{\eta^2}} - \eta \int_{\eta}^{\infty} e^{-u^2} du \right] \qquad (245)$$

$$= \left(\frac{J_s a}{\bar{D}} \right) \left(\sqrt{\frac{4}{\pi}} \right) \left[\frac{\sqrt{\tau}}{e^{\eta^2}} - (2\eta\sqrt{\tau}) \int_{\eta}^{\infty} e^{-u^2} du \right] \qquad (246)$$

$$(c - c_{ini}) = \left(\frac{J_s a}{\bar{D}} \right) \left(\sqrt{\frac{4}{\pi}} \right) \left[\frac{\sqrt{\tau}}{\exp\left(\frac{Y^2}{4\tau} \right)} - Y \int_{u=\frac{Y}{2\sqrt{\tau}}}^{u=\infty} e^{-u^2} du \right] \qquad (247)$$

Also,

$$(c - c_{ini}) = \left(\frac{J_s a}{\bar{D}} \right) \left(\sqrt{\frac{4}{\pi}} \right) \left[\frac{\sqrt{\tau}}{\exp\left(\frac{Y^2}{4\tau} \right)} - \left(\frac{\sqrt{\pi}}{2} \right) Y \left(\frac{2}{\sqrt{\pi}} \int_{u=\frac{Y}{2\sqrt{\tau}}}^{u=\infty} e^{-u^2} du \right) \right] \qquad (248)$$

$$(c - c_{ini}) = \left(\frac{J_s a}{\bar{D}} \right) \left(\sqrt{\frac{4}{\pi}} \right) \left[\frac{\sqrt{\tau}}{\exp\left(\frac{Y^2}{4\tau} \right)} - \left(\frac{\sqrt{\pi}}{2} \right) Y \, erfc\left(\frac{Y}{2\sqrt{\tau}} \right) \right] \qquad (249)$$

where (the complementary error function of

$$\left(\frac{Y}{2\sqrt{\tau}}\right) = erfc\left(\frac{Y}{2\sqrt{\tau}}\right) = \left(\frac{2}{\sqrt{\pi}}\right)\int\limits_{u=\frac{Y}{2\sqrt{\tau}}}^{u=\infty} e^{-u^2}\,du \tag{250}$$

The equation (249) is now written as

$$\left[\frac{(c-c_{ini})\bar{D}}{J_s a}\right] = \left(\frac{2}{\sqrt{\pi}}\right)\left[\frac{\sqrt{\tau}}{\exp\left(\frac{Y^2}{4\tau}\right)} - \left(\frac{\sqrt{\pi}}{2}\right)Y\,erfc\left(\frac{Y}{2\sqrt{\tau}}\right)\right] \tag{251}$$

(valid for $\tau > 0$; $0 \le Y \le 0.1$ to satisfy the condition of short distance penetration by lithium, i.e. $Li^+ + e^-$ pair, from the electrolyte-active material interfacial surface into the particle).

At the particle surface, i.e., $y = 0$ or $Y = \frac{y}{a} = 0$, $c = c_s$, Eq. (251) becomes

$$\left[\frac{(c_s - c_{ini})\bar{D}}{J_s a}\right] = \left(\frac{2}{\sqrt{\pi}}\right)\left[\frac{\sqrt{\tau}}{1} - \frac{\sqrt{\pi}}{2}(0)erfc(0)\right] \tag{252}$$

$$= \left(\frac{2}{\sqrt{\pi}}\right)\left[\sqrt{\tau} - \frac{\sqrt{\pi}}{2}(0)(1)\right] = \left(\frac{2}{\sqrt{\pi}}\right)\sqrt{\tau} \tag{253}$$

$$= \left(\frac{2}{\sqrt{\pi}}\right)\sqrt{\tau} \tag{254}$$

Notice that the particle surface concentration, i.e., $(c_s - c_{ini})$ is proportional to $\sqrt{\tau}$. Expressing the equations (251) and (254) as follows,

$$\left[\frac{(c-c_{ini})\bar{D}}{J_s a}\right] = \left[\frac{(x-x_{ini})\rho_{cathode}\bar{D}}{M_{cathode}(J_s a)}\right] = \left(\frac{2}{\sqrt{\pi}}\right)\left[\frac{\sqrt{\tau}}{\exp\left(\frac{Y^2}{4\tau}\right)} - \left(\frac{\sqrt{\pi}}{2}\right)Y\,erfc\left(\frac{Y}{2\sqrt{\tau}}\right)\right] \tag{255}$$

$$\left[\frac{(c_s-c_{ini})\bar{D}}{J_s a}\right] = \left[\frac{(x_s-x_{ini})\rho_{cathode}\bar{D}}{M_{cathode}(J_s a)}\right] = \left(\frac{2}{\sqrt{\pi}}\right)\sqrt{\tau} \tag{256}$$

At the time, $t = t_s^{sat'd}$, when the lithium concentration at the particle surface, $r = a$ or $Y = 1$ reaches the saturation level for a given cathode active material of density, $\rho_{cathode}$, and molecular weight, $M_{cathode}$; then, $c_s = c_s^{sat'd}$ and $x_s = x_s^{sat'd}$ and $\tau = \tau_s^{sat'd} = \dfrac{\bar{D} t_s^{sat'd}}{a^2}$.

Equation (256) is rewritten for the cathode active material surface saturation with lithium.

$$\left[\frac{\left(c_s^{sat'd} - c_{ini} \right) \bar{D}}{J_s a} \right] = \left[\frac{\left(x_s^{sat'd} - x_{ini} \right) \rho_{cathode} \bar{D}}{M_{cathode} \left(J_s a \right)} \right] = \left(\frac{2}{\sqrt{\pi}} \right) \sqrt{\tau_s^{sat'd}} \tag{257}$$

Note that in Eqs. (255) and (256), x = *g-moles* of Li per *g-mole* of cathode active material.

Equation (255) can be used to predict $\left[\dfrac{\left(c - c_{ini} \right) \bar{D}}{J_s a} \right]$ or $\left[\dfrac{\left(x - x_{ini} \right) \rho_{cathode} \bar{D}}{M_{cathode} \left(J_s a \right)} \right]$ as a function of Y

at each τ and Eq. (256) should be used to predict $\left[\dfrac{\left(c_s - c_{ini} \right) \bar{D}}{J_s a} \right] = \left[\dfrac{\left(x_s - x_{ini} \right) \rho_{cathode} \bar{D}}{M_{cathode} \left(J_s a \right)} \right]$ as a

function of τ. For a fixed value of $t_s^{sat'd}$, e.g., $t_s^{sat'd} = 0.001$ second for the lithium concentration at the particle surface to reach $\left(x_s^{sat'd} - x_{ini} \right)$, one can compute $\left(J_s a \right)$ from Eq. (257). Then, one can compute J_s corresponding to a value of the spherical active material particle radius, a. One may call this lithium-ion flux at the electrolyte-active material interface $J_s^{sat'd}$, i.e., $J_s = J_s^{sat'd}$, lithium ion flux required at the particle surface for the lithium concentration at the particle surface to reach the saturated level in a desired period of time, $t_s^{sat'd}$ or $\tau_s^{sat'd}$. One can then compute the electrolyte-active material interfacial current density to satisfy this requirement, i.e., $\left| i_s^C \right| = J_s^{sat'd} F$ for a selected cathode active material particle radius. It is, here, reminded that the cell should be considered discharged when the lithium concentration inside the particle at its surface reaches the saturation level.

The cathode coulomb efficiency, U, to store lithium in a particle of a cathode active material, (see Eq. 168), is given below.

$$U = \left[\frac{3 \tau_s^{sat'd}}{\left\{ \dfrac{\bar{D} \left(x_s^{sat'd} - x_{ini} \right) \rho_{cathode}}{\left(J_s a \right) M_{cathode}} \right\}} \right] \tag{258}$$

Inserting the expression for $\left\{ \dfrac{\bar{D} \left(x_s^{sat'd} - x_{ini} \right) \rho_{cathode}}{\left(J_s a \right) M_{cathode}} \right\}$ from Eq. (257) into Eq. (258) leads to

$$U = \left(\frac{3\sqrt{\pi}}{2}\right)\sqrt{\tau_s^{sat'd}} \tag{259}$$

So, one can compute the cathode coulomb efficiency, U, from Eq. (259) for a $\tau_s^{sat'd} = \dfrac{\bar{D}t_s^{sat'd}}{a^2}$ for a fixed $t_s^{sat'd}$ value for the various values of the cathode active material particle radius, a, to observe the effect of the particle dimension on the coulomb efficiency by the use of Eq. (259) derived for the short-time cell discharge period.

Properties of $erf(\eta)$ and $erfc\left(\eta = \dfrac{Y}{2\sqrt{\tau}}\right)$; and some of their tabulated values are given below for their use in Eq. (255).

$$erf(\eta) = \frac{2}{\sqrt{\pi}}\int_0^\eta e^{-u^2}\,du, \quad erfc(\eta) = 1 - erf(\eta) = \left(\frac{2}{\sqrt{\pi}}\right)\int_\eta^\infty e^{-u^2}\,du$$

$$erf(\eta) = \frac{2}{\sqrt{\pi}}\left(\eta - \frac{\eta^3}{3\cdot 1!} + \frac{\eta^5}{5\cdot 2!} - \frac{\eta^7}{7\cdot 3!} + \cdots\right)$$

$$erfc(\eta) = 1 - \frac{2}{\sqrt{\pi}}\left(\eta - \frac{\eta^3}{3\cdot 1!} + \frac{\eta^5}{5\cdot 2!} - \frac{\eta^7}{7\cdot 3!} + \cdots\right)$$

$$\boxed{erf(-\eta) = -erf(\eta), \quad erf(0) = 0, \quad erf(\infty) = 1; \quad erfc(0) = 1, \quad erfc(\infty) = 0.}$$

Also, $erf(\eta) \square\ 1 - \dfrac{e^{-\eta^2}}{\sqrt{\pi}\eta}\left(1 - \dfrac{1}{2\eta^2} + \dfrac{1\cdot 3}{\left(2\eta^2\right)^2} - \dfrac{1\cdot 3\cdot 5}{\left(2\eta^2\right)^3} + \cdots\right)$

$$erfc(\eta) \square\ \frac{e^{-\eta^2}}{\sqrt{\pi}\eta}\left(1 - \frac{1}{2\eta^2} + \frac{1\cdot 3}{\left(2\eta^2\right)^2} - \frac{1\cdot 3\cdot 5}{\left(2\eta^2\right)^3} + \cdots\right)$$

Table 1.   Some Values for the Error and Complementary Error Functions

$\eta = \dfrac{Y}{2\sqrt{\tau}}$	$erf(\eta)$	$erfc(\eta)$
0.00	0.00000	1.000000
0.05	0.056372	0.943628
0.10	0.112463	0.887537
0.15	0.167996	0.832004

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0.20	0.222703	0.777297
0.25	0.276326	0.723674
0.30	0.328627	0.671373
0.35	0.379382	0.620618
0.40	0.428392	0.571608
0.45	0.475482	0.524518
0.50	0.5205	0.479500
0.55	0.563323	0.436677
0.60	0.603856	0.396144
0.65	0.642029	0.357971
0.70	0.677801	0.322199
0.75	0.711156	0.288844
0.80	0.742101	0.257899
0.85	0.770668	0.229332
0.90	0.796908	0.203092
0.95	0.820891	0.179109
1.00	0.842701	0.157299
1.10	0.880205	0.119795
1.20	0.910314	0.089686
1.30	0.934008	0.065992
1.40	0.952285	0.047715
1.50	0.966105	0.033895
1.60	0.976348	0.023652
1.70	0.98379	0.016210
1.80	0.989091	0.010909
1.90	0.99279	0.00721
2.00	0.995322	0.004678
2.10	0.997021	0.002979
2.20	0.998137	0.001863
2.30	0.998857	0.001143
2.40	0.999311	0.000689
2.50	0.999593	0.000407
2.60	0.999764	0.000236
2.70	0.999866	0.000134
2.80	0.999925	7.5E-05
2.90	0.999959	4.1E-05
3.00	0.999978	2.2E-05

4.1.7 Determination of Voltage Loss Associated with the Diffusion Transport of Lithium, i.e., the Lithium Diffusion Voltage Polarization in the Cathode Active Material

Diffusivity of lithium ion in the cathode solid-state active material as the solvent for the solute, lithium ion is related to its ionic conductivity, κ_+^C, via the following expression [10]:

$$\bar{D}_{\text{Li}^+} = \left[\frac{RT\kappa_+^C}{\left(\bar{c}_{\text{Li}^+}F\right)F} \right] \tag{260}$$

(the Nernst-Einstein relation)

Subtracting Eq. (162) from Eq. (163) leads to:

$$\left[\frac{\left(c_s - c_{center}\right)\bar{D}}{J_s a} \right] = \left[\frac{\left(x_s - x_{center}\right)\bar{D}}{J_s a}\left(\frac{\rho_{\text{cathode}}}{M_{\text{cathode}}} \right) \right]$$

$$= \left[0.5 + 2\sum_{n=1}^{n=\infty} \left\{ \frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)\sin\left(a\alpha_n\right)} - \frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2} \right\} \right] \tag{261}$$

Substitution for $\bar{D}_{\text{Li}^+}\left(=\bar{D}\right)$ from Eq. (260) into Eq. (261) and simplification, with $J_s = \dfrac{\left|i_s^C\right|}{F}$,

leads to

$$\left[\frac{\left(\frac{c_s - c_{center}}{\bar{c}} \right)\left(\frac{RT}{F} \right)}{\left(\frac{\left|i_s^C\right|a}{\kappa_+^C} \right)} \right] = \left[\frac{\left(\frac{x_s - x_{center}}{\bar{x}} \right)\left(\frac{RT}{F} \right)}{\left(\frac{\left|i_s^C\right|a}{\kappa_+^C} \right)} \right]$$

$$= \left[0.5 + 2\sum_{n=1}^{n=\infty} \left\{ \frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)\sin\left(a\alpha_n\right)} - \frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2} \right\} \right] \tag{262}$$

where the lithium concentration $\bar{x}$ averaged over the dimensionless particle radius at any time τ is given by

$$\bar{x} = \int_0^{1.0} x\, d\xi \tag{263}$$

Note that x, at any time τ, is to be determined as a function of ξ using Eq. (159). Then, Eq. (263) is to be employed to obtain $\bar{x}$ at each τ.

Defining $\left[\left(\dfrac{x_s - x_{center}}{\bar{x}}\right)\left(\dfrac{RT}{F}\right)\right] = \left[\left(\dfrac{c_s - c_{center}}{\bar{c}}\right)\left(\dfrac{RT}{F}\right)\right] = \left(\Delta V_D\right)^C$, voltage loss associated with

the lithium ion diffusion inside a cathode active material spherical particle due to the situation of x_s and x_{center} being different from $\bar{x}$; then, Eq. (262) is written as

$$\left[\frac{\left(\Delta V_D\right)^C}{\left(\dfrac{\left|i_s^C\right| a}{\kappa_+^C}\right)}\right] = \left[0.5 + 2\sum_{n=1}^{n=\infty}\left\{\frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)\sin\left(a\alpha_n\right)} - \frac{\exp\left(-\tau\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2}\right\}\right] \tag{264}$$

where $\left|i_s^C\right| = $ constant electrolyte-cathode active material interfacial surface current density during

the cell discharge period, $a = $ cathode material particle radius, and $\kappa_+^C = $ lithium ion

conductivity in the cathode active material. Equation (264) can be used to determine $\left(\Delta V_D\right)^C$, voltage loss associated with the lithium ion diffusion in the cathode active material as a function of τ during the cell discharge period. For the general application of the result in Eq. (264) for the spherical particles of a cathode active material, it is suggested that the dimensionless

lithium-diffusion-voltage loss, $\left[\dfrac{\left(\Delta V_D\right)^C}{\left(\dfrac{\left|i_s^C\right| a}{\kappa_+^C}\right)}\right]$, should be calculated as a function of τ and a plot of

$\left[\dfrac{\left(\Delta V_D\right)^C}{\left(\dfrac{\left|i_s^C\right| a}{\kappa_+^C}\right)}\right]$ vs. τ be developed.

4.1.8   Evaluation of the Effect of Lithium Storage on the Cell Reversible Voltage

The cell reversible voltage is given by Eq. (144). If the standard-state lithium composition, x^o, is unknown, one may eliminate it from the cell voltage expression by first writing Eq. (144) for a known value of $E_{rev,1}^{cell}$ at a lithium composition, $x = x_1$ value and then subtracting the expression for $E_{rev,1}^{cell}$ from Eq. (144) to obtain, on simplification,

$$\left[\frac{E_{rev}^{cell} - E_{rev,1}^{cell}}{\left(\dfrac{RT}{F}\right)}\right] = -\ln\left[\left(\frac{\gamma_{Li}}{\gamma_{Li,1}}\right)\left(\frac{x}{x_1}\right)\right] \tag{265}$$

Note: The value of the function within [ ] should be ≥ 1.

Notice that the reversible cell voltage loss can be determined as a function of x provided $\left(\dfrac{\gamma_{Li}}{\gamma_{Li,1}}\right)$

is known as a function of x or $\left(\dfrac{x}{x_1}\right)$ during the cell discharge period. To evaluate the effect of lithium storage on the reversible voltage, $x = x_s$ (at the particle surface); therefore, Eq. (265) becomes

$$\left[\frac{E_{rev}^{cell} - E_{rev,1}^{cell}}{\left(\dfrac{RT}{F}\right)}\right] = -\ln\left[\left(\frac{\gamma_{Li}}{\gamma_{Li,1}}\right)\left(\frac{x}{x_1}\right)\right] = F(x_s) \qquad (266)$$

x_s should be computed from the following equation derived from Eq. (163).

$$x_s = x_{ini} + \frac{(J_s a) M_{cathode}}{\bar{D} \rho_{cathode}}\left[3\tau + 0.2 - 2\sum_{n=1}^{n=\infty} \frac{\exp\left(-\tau(a\alpha_n)^2\right)}{(a\alpha_n)^2}\right] \qquad (267)$$

Recognizing $J_s = \dfrac{\left|i_s^C\right|}{F}$, Eq. (267) is now expressed as

$$x_s = x_{ini} + \left(\frac{\left|i_s^C\right| a}{F}\right)\frac{M_{cathode}}{\bar{D}\rho_{cathode}}\left[3\tau + 0.2 - 2\sum_{n=1}^{n=\infty} \frac{\exp\left(-\tau(a\alpha_n)^2\right)}{(a\alpha_n)^2}\right] \qquad (268)$$

If the correlation for γ_{Li}, activity coefficient of Li (in fact, Li$^+$), as a function of the intercalated or moveable lithium ion composition is not available; then, $F(x_s)$ at an $x_s = x_1 + \delta x$ can be obtained from the following derived Taylor series, provided δx has such value that γ_{Li} (at an $x_s = x_1 + \delta x$) does not differ from $\gamma_{Li,1}$ at x_1 to any significance.

$$F(x_s) = -\left[\left(\frac{\delta x}{x_1}\right) - \left(\frac{1}{2!}\right)\left(\frac{\delta x}{x_1}\right)^2 + \left(\frac{2}{3!}\right)\left(\frac{\delta x}{x_1}\right)^3 - \left(\frac{6}{4!}\right)\left(\frac{\delta x}{x_1}\right)^4 + R_5\right] \qquad (269)$$

where the remainder R_5 is given by

$$R_5 = \left(\frac{24}{5!}\right)\left(\frac{\delta x}{\xi}\right)^5 \qquad (270)$$

(the Lagrange's form)

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$$R_5 = \left[\frac{\{(x_1 + \delta x) - \xi\}^4}{\xi^5} \right] \delta x \tag{271}$$

(the Cauchy's form)

with $x_1 < \xi < (x_1 + \delta x)$.

To observe the effect of lithium storage in the cathode active material particles on the reversible voltage, $F(x_s)$ should be computed as a function of τ using Eq. (268); then, the plot of

$\left[\dfrac{E_{rev}^{cell} - E_{rev,1}^{cell}}{\left(\dfrac{RT}{F} \right)} \right]$ vs. τ should be developed.

Equation (256) developed to predict the lithium surface concentration in a cathode active material for the condition of lithium penetration in a short distance from the electrolyte-active material interface may also be used, in approximation, to compute the voltage loss associated with the lithium diffusion inside the cathode active material particles and to observe the effect of lithium storage on the cell reversible voltage.

The lithium ion diffusivity $\bar{D}$ in Eq. (256) is expressed in terms of the lithium ion conductivity κ_+^C using the Nernst-Einstein relation, Eq. (260) to obtain:

$$\left[\frac{(c_s - c_{ini}) RT \kappa_+^C}{(\overline{c_{Li^+}} F) F} \right] \left(\frac{1}{J_s a} \right) = \frac{(x_s - x_{ini}) \rho_{cathode}}{M_{cathode}(J_s a)} \cdot \frac{RT \kappa_+^C}{(\overline{c_{Li^+}} F) F}$$
$$= \left(\frac{2}{\sqrt{\pi}} \right) \sqrt{\tau} = 1.1284 \sqrt{\tau} \tag{272}$$

Because $\overline{c_{Li^+}} = x_{Li^+, avg} \dfrac{\rho_{cathode}}{M_{cathode}}$; so,

$$\frac{(x_s - x_{ini}) \rho_{cathode}}{M_{cathode}(J_s a)} \cdot \frac{1}{x_{Li^+, avg} \dfrac{\rho_{cathode}}{M_{cathode}}} \cdot \frac{RT \kappa_+^C}{(F \cdot F)} = 1.1284 \sqrt{\tau} \tag{273}$$

$$\left(\frac{x_s - x_{ini}}{x_{avg}} \right) \cdot \left(\frac{RT}{F} \right) \cdot \frac{\kappa_+^C}{F(J_s a)} = 1.1284 \sqrt{\tau} \tag{274}$$

$$\left[\frac{\left(\dfrac{x_s - x_{ini}}{x_{avg}}\right)\dfrac{RT}{F}}{\dfrac{\left|i_s^C\right|a}{\kappa_+^C}}\right] = 1.1284\sqrt{\tau} \tag{275}$$

Note that the left-side of Eq. (275) is taken to be the measure of voltage change at any time $\tau = \dfrac{\overline{D}t}{a^2}$. It is suggested that the result, Eq. (275) should be used only for τ values such that

$$Y = Y_m = \frac{\delta_m}{a} = \frac{4\sqrt{\overline{D}t}}{a} = 4\sqrt{\frac{\overline{D}t}{a^2}} = 4\sqrt{\tau} \leq 0.1 \quad \text{to satisfy the condition of short penetration of Li}^+ \text{ (as}$$

$\text{Li}^+ + e^-$) in the cathode active material spherical particle from the electrolyte-active material particle interface. We may express Eq. (275) as

$$\left[\frac{\left(\dfrac{x_s - x_{ini}}{x_{avg}}\right)\dfrac{RT}{F}}{\dfrac{\left|i_s^C\right|a}{\kappa_+^C}}\right] = \left[\frac{\left(\Delta V_D\right)_s^C}{\dfrac{\left|i_s^C\right|a}{\kappa_+^C}}\right] = 1.1284\sqrt{\tau} \tag{276}$$

where $\left(\Delta V_D\right)_s^C$ is indicative of the voltage change associated with the lithium ion diffusion inside the cathode active material.

From Eq. (256), one can obtain

$$x_s = x_{ini} + \left(\frac{2}{\sqrt{\pi}}\sqrt{\tau}\right)(J_s a)\left(\frac{M_{cathode}}{\rho_{cathode}\overline{D}}\right) = x_{ini} + \left(2\sqrt{\frac{\tau}{\pi}}\right)\left(\frac{\left|i_s^C\right|a}{F}\right)\left(\frac{M_{cathode}}{\rho_{cathode}\overline{D}}\right) \tag{277}$$

Equation (277) may also be used to show the effect of transient accumulation of lithium inside the cathode active material particles at a fixed current density $\left|i_s^C\right|$ on the reversible voltage of the cell through the application of Eq. (266) or (143).

4.1.9   Further Treatment of the Reversible Potential of the Lithium-Based Cell, Eq. (144)

From Eq. (144), one can obtain the following equation:

$$E_{rev} = E_{rev}^o + \frac{RT}{F}\ln\left(x^o\right) - \frac{RT}{F}\left\{\ln\left[\gamma_{\text{Li-in M}_y\text{Pc}}\right] + \ln x\right\} \tag{278}$$

After entering the cathode active material through the electrolyte-active material particle interface, lithium ion moves, with its "captured electron" present in its near vicinity. This

situation may be represented as: $Li^+ + e^- \; \square \quad Li$ inside the cathode active material acting as the solid-state solvent. Then, the following expression, similar to that for a liquid-phase electrolytic solution [10], is written as an approximation to $\ln\left[\gamma_{\text{Li-in } M_y\text{Pc}}\right]$,

$$\ln\left[\gamma_{\text{Li-in } M_y\text{Pc}}\right] = \underbrace{\left[\frac{z_+ z_- \alpha\sqrt{I}}{1 + Ba\sqrt{I}}\right]}_{I} + \underbrace{\beta_1 x}_{II} \tag{279}$$

Term I of the right-hand side of Eq. (279) is assumed to account for the lithium ion interactions with the surrounding charges through the coulomb type (long-range) forces and the second term II is assumed to account for the short-range interactions of lithium ion with the surrounding charges.

$$\text{Term(I)} = \frac{z_+ z_- \alpha\sqrt{I}}{1 + Ba\sqrt{I}} = \frac{(+1)(-1)\alpha\sqrt{I}}{1 + Ba\sqrt{I}} = \frac{-\alpha\sqrt{I}}{1 + Ba\sqrt{I}} \tag{280}$$

where $a =$ lithium-ion diameter; parameter, $B = \sqrt{\dfrac{2\rho_o}{\varepsilon RT}} \cdot F; \alpha = \dfrac{\sqrt{2\rho_o}\,F^3}{8\pi L\left(\varepsilon RT\right)^{1.5}}$; and

$I = \dfrac{1}{2}\sum_i z_i^2 m_i = \dfrac{1}{2}\left[z_{\text{Li}^+}^2 m_{\text{Li}^+} + z_{e^-}^2 m_{e^-}\right] = \dfrac{1}{2}\left[(1)m + (1)m\right] = m =$ molality of the intercalated lithium

in the solid state cathode material as solvent $= \dfrac{x}{M_{cathode}}$. $L =$ Avogadro's number $= 6.0223 \times 10^{23}$

per g-mole, $F =$ Faraday's constant $= 96487$ coulomb per g-equivalent, $R =$ gas constant $= 8.314\, J / mol \cdot K$, $T =$ temperature $\left[K\right]$, $\varepsilon =$ permittivity of the solid-state cathode active material $= D\varepsilon_o =$ (dielectric constant of the solid-state cathode active material) (permittivity of free space), $\varepsilon_o = 8.8542 \times 10^{-14}\, \dfrac{Farad}{cm} = 8.8542 \times 10^{-14}\, \dfrac{coulomb\; volt^{-1}}{cm}$,

$x = \dfrac{g\text{-}mole \text{ of the mobile or intercalated lithium ions}}{g\text{-}mole \text{ of the cathode active material}}$, $M_{cathode} =$ mol. wt. of the cathode active material, $\rho_o =$ density of the cathode active material.

Using the information in Eq. (280), Eq. (279) is expressed as:

$$\ln\left[\gamma_{\text{Li-in } M_y\text{Pc}}\right] = \left[\frac{-\dfrac{a}{\sqrt{M_{cathode}}}\sqrt{x}}{1 + \left(\dfrac{Ba}{\sqrt{M_{cathode}}}\right)\sqrt{x}}\right] + \beta_1 x \tag{281}$$

Inserting for $\ln\left[\gamma_{\text{Li-in M}_y\text{Pc}}\right]$ into Eq. (278) leads to:

$$E_{rev} = \left[E_{rev}^o + \frac{RT}{F}\ln\left(x^o\right)\right] + \frac{RT}{F}\left\{\frac{\left(\dfrac{a}{\sqrt{M_{cathode}}}\right)\sqrt{x}}{1+\left(\dfrac{Ba}{\sqrt{M_{cathode}}}\right)\sqrt{x}}\right\} - \frac{RT}{F}\ln x - \left(\frac{RT}{F}\beta_1\right)x \quad (282)$$

Equation (282) is now expressed as:

$$E_{rev} + \frac{RT}{F}\left[\ln x - \left\{\frac{\left(\dfrac{a}{\sqrt{M_{cathode}}}\right)\sqrt{x}}{1+\left(\dfrac{Ba}{\sqrt{M_{cathode}}}\right)\sqrt{x}}\right\}\right] = \left[E_{rev}^o + \frac{RT}{F}\ln\left(x^o\right)\right] - \left(\frac{RT}{F}\beta_1\right)x \quad (283)$$

This result suggests that one should experimentally determine E_{rev} vs. x, i.e.,open-circuit voltage vs. x data at the cathode active material particle equilibrium state at each x value at a fixed temperature. Then, one should plot

$$\left(E_{rev} + \frac{RT}{F}\left[\ln x - \left\{\frac{\left(\dfrac{a}{\sqrt{M_{cathode}}}\right)\sqrt{x}}{1+\left(\dfrac{Ba}{\sqrt{M_{cathode}}}\right)\sqrt{x}}\right\}\right]\right)$$ vs. x on a linear graph paper. If the plot is predicted

to be a straight line with slope $=\left(-\dfrac{RT}{F}\right)\beta_1$; then, β_1 is determined for its application in Eq. (281), and, hence, in Eq. (278) for future computations of E_{rev} vs. x at the temperature for which β_1 has been estimated. Note that x^o is the x value to be selected corresponding to a E_{rev}^o value and also x should be greater than x^o value.

4.1.10 Fractional Utilization of a Cathode Active-Material Particle as a Function of Time at a Constant Electrolyte-Active Material Interfacial Current Density

The fractional utilization of the cathode active material, U, is defined as a function of time as follows.

$$U = \frac{\left(\begin{array}{l}\text{amount of lithium transferred into a cathode active material particle of} \\ \text{radius, } a, \text{ in time, } t, \text{ during the cell discharge period at a constant lithium-} \\ \text{ion flux or current density at the electrolyte-active material interface}\end{array}\right)}{\left(\begin{array}{l}\text{amount of intercalated lithium the active material} \\ \text{particle of radius, } a, \text{ can hold up to the saturation level}\end{array}\right)} \quad (284)$$

$$= \frac{\left(4\pi a^2 J_s\right)t}{\dfrac{4}{3}\pi a^3\left[\left(x^{sat'd} - x_{ini}\right)\dfrac{\rho_{cathode}}{M_{cathode}}\right]} \quad (285)$$

$$= \frac{3J_s t}{a\left[\left(x^{sat'd} - x_{ini}\right)\dfrac{\rho_{cathode}}{M_{cathode}}\right]} = \frac{3i_s^C t}{Fa\left[\left(x^{sat'd} - x_{ini}\right)\dfrac{\rho_{cathode}}{M_{cathode}}\right]} \quad (286)$$

where $J_s =$ lithium ion flux and $i_s^C =$ constant electrolyte active material interfacial current density.

Note that $'t'$ should be $\leq t_s^{sat'd}$, the time in which the lithium concentration at the particle surface reaches the saturation level, i.e., $\left(x_s - x_{ini}\right)$ becomes $\left(x^{sat'd} - x_{ini}\right)$. This $t_s^{sat'd}$ can be determined using Eq. (169) in the following form.

$$\left(\frac{\bar{D}\left(x_s^{sat'd} - x_{ini}\right)\rho_{cathode}}{\left(J_s a\right)M_{cathode}}\right) = \left(\frac{\bar{D}F\left(x^{sat'd} - x_{ini}\right)\rho_{cathode}}{i_s^C a M_{cathode}}\right)$$
$$= \left[3\tau_s^{sat'd} + 0.2 - 2\sum_{n=1}^{n=\infty}\frac{\exp\left(-\tau_s^{sat'd}\left(a\alpha_n\right)^2\right)}{\left(a\alpha_n\right)^2}\right] \quad (287)$$

One should determine $\tau_s^{sat'd}$ by solving Eq. (287) for a fixed value of i_s^C. Then, through the definition of $\tau_s^{sat'd} = \dfrac{\bar{D}t_s^{sat'd}}{a^2}$; one determine $t_s^{sat'd} = \dfrac{a^2\tau_s^{sat'd}}{\bar{D}}$.

5. CONCLUSIONS

To help explain AFRL/RZPS in-house experimental results on lithium-based cells using dilithium phthalocyanine as the active cathode material, Dr. Sarwan Sandhu from the University of Dayton was tasked to develop a model formulation and simulation for these types of electrochemical cells.   The experimental and modeled cells consisted of lithium foil anodes, lithium tetrafluoroborate in poly(ethylene oxide) electrolytes, and metal phthalocyanine based cathodes.   The developed formulation covered the various subtopics relating to the performance and processes occurring at the cell cathode, electrolyte separator, and cell anode.

Determination of the transient cathode performance under discharge was treated extensively due to the assumed solid-state diffusion-limited cell behavior.   Boundary conditions of a constant concentration or current density on the cathode active material particles were used.   Solutions consisted of the cathode performance for a given surface concentration or for a given cell current density.

The reversible cathode potential was determined as a function of the amount of lithium intercalated into the phthalocyanine material.

Equations for the electrode kinetics at the cell cathode and anode were developed to help determine the cathode overpotentials or activation polarization losses occurring during cell discharge.

Further effort is needed on using the developed formulation and applying it to existing and future experimental results on lithium-based phthalocyanine solid-state cells.

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